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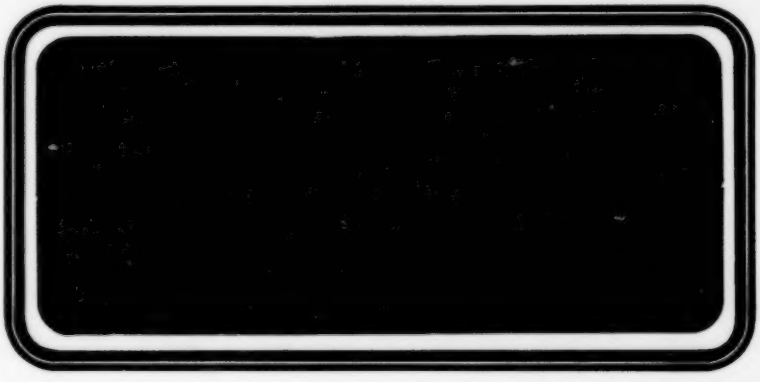

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The Canada–Alberta Forest Resource Development Agreement is funded equally by the governments of Canada and Alberta, from April 1, 1984, to March 31, 1989.

Its primary objectives are to ensure the long-term availability of timber supplies; to optimize timber uses; and to contribute to the growth and diversification of Alberta's economy.

The Agreement comprises three programs: Reforestation; Applied research, technology transfer and opportunity identification; and Public information, evaluation and administration. These programs are managed by a joint Directorate and are implemented by Forestry Canada and the Alberta Forest Service.

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Ses objectifs principaux sont assurer la disponibilité à long terme de réserves de bois; optimiser leur utilisation; et contribuer à la croissance et la diversification de l'économie de la province.

L'Entente comprend trois programmes: Reboisement; Recherche appliquée, transferts de connaissances techniques et relevé des occasions; et Information, évaluation et administration. Ces programmes sont gérés par un Bureau de direction conjoint, et mis en oeuvre par Forêts Canada et le Service forestier de l'Alberta.

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POTENTIAL FOR ENZYMATIC LIGNIN-BASED ADHESIVES STATE OF THE ART REVIEW

Forintek Canada Corp.[1]

1987

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EXECUTIVE SUMMARY

Processing lignocellulosic materials into cellulose pulps and chemicals produces large quantities of lignins as by-products. The numerous attempts to utilize these lignins as adhesives have resulted in only very limited industrial success. Major obstacles have been the inherent complex and hetrogeneous structure of lignin and the lack of a thorough understanding of the relationship between these structure and their performance capabilities as adhesives. The projected future availability of lignins from steam explosion and organosolv processes raises the question whether these will be more suitable as adhesive materials. This report is intended to provide a perspective of the present status and future potential of lignin as an adhesive with special emphasis on lignin for enzymatic type processes. Its terms of reference encompass a review of the historical development of lignin based resins with identification of existing and potential sources of different lignin types which are or may become available; a review of adhesive process requirements related to the manufacture of specific wood composites such as oriented strandboard, plywood, parallam and glue-laminated lumber and an indication of new technology which may help overcome limitations in application and cure of lignin-based adhesives.

The study is divided into three parts. The first covers the historical developments in lignin adhesives which primarily relate to spent sulphite lignin (SSL) and Draft lignin areas as applied to reconstituted wood products. Relevant scientific publications are identified and abstract summaries presented. Assessment of these adhesive development first is provided in terms of lignin-based systems not in combination with synthetic adhesives, but includes the use of modifiers and catalysts. The status of lignin-based wood adhesives in combination with UF and PF then are discussed. This is and area of activity where substantial amounts of research and development has and still is occurring. A separate discussion is provided on the so far, limited work undertaken with bioconversion lignins as adhesives in wood products:

The second part considers physical and chemical requirements of adhesive necessay to satisfy application and processing needs for various glued wood products. Analysis is presented of polymer and adhesive properties important to the application, processing and bond performance aspects of glued composite manufacture. These include properties such as reactive functionality, molecular weight, polymer solubility, flow, wetting and cure time. Discussion is included of how well present and future lignin adhesive candidates will fit in these requirements.

The third part deals with the potential of lignin adhesives in the future while recognizing the present problems restricting their commercial usage. It was concluded from the literature and knowledge

gained through research experience that the lack of uniformity in lignins from different pulping sources, the limited information about lignin properties, especially from steam explosion and organosolv processes and the restricted number of reactive sites on lignin, were the major impediments to lignins use as exterior grade adhesives. In the near future, it is recommended that research emphasis be directed towards:

- further developing PF-lignin adhesive combinations since these have the greatest opportunity for commercial success.
- fully characterizing steam explosion and organosolv lignin materials
- improving lignin uniformity through fractionation and separation techniques
- enhancing chemical reactivity primarily through the development of appropriate demethylation reactions
- utilizing improved application technology (i.e. foaming)
- evaluating steam pressing technology to enhance cure speed of lignin-based adhesives.

TABLE OF CONTENTS

		Page
	Executive Summary	i
	List of Tables	v
	List of Figures	vi
1.0	Introduction	1
2.0	Staff Team	5
3.0	Part 1 - An overview of the use of various lignins in adhesives for wood composites	6
3.1	Introduction	6
3.2	Section A - Lignin-based wood adhesives without combination with UF or PF	13
3.2.1	Comments	13
3.2.2	Literature review	15
3.3	Section B - Lignin-based wood adhesives in combination with UF or PF	23
3.3.1	Comments	23
3.3.2	Literature review	25
3.4	Section C - Bioconversion lignins (steam exploded, acid hydrolysis and enzyme lignins) as adhesives in wood products	37
3.4.1	Comments	37
3.4.2	Literature review	38
3.5	Primary researchers and organizations currently active in lignin adhesive	40
4.0	Part II - Wood adhesive application and property requirements	42
4.1	Adhesive process requirements for specific wood products	42
4.1.1	Plywood/LVL	42
4.1.2	Waferboard/OSB	46
4.1.3	Particleboard	48
4.1.4	Medium density fiberboard (MDF)	49
4.1.5	Laminated lumber products	50
4.1.6	Comparative adhesive usages	51

4.2 Polymer and adhesive properties influencing bond performance 54

4.2.1 Polymer properties 54
4.2.1.1 Reactive functionality 54
4.2.1.2 Molecular weight and molecular weight distribution 55
4.2.1.3 Solubility 61
4.2.1.4 Thermal softening 61

4.2.2 Adhesive properties 63
4.2.2.1 Viscosity 63
4.2.2.2 Flow and wetting 63
4.2.2.3 Cure time and temperature 64

5.0 Future Potential of lignin-based adhesives 66

5.1 Isolation and uniformity 67
5.2 Standards development 68
5.3 Modification to increase reactivity 68
5.4 Application technology 69
5.5 Processing technology 69
5.6 Survey of opinions on lignin adhesives in future 70
5.7 Alberta's and Canada's R&D capabilities the field of lignin-based adhesive developments 72

6.0 Conclusions and Recommendations 72

7.0 General References 75

LIST OF TABLES

Table 1	Current Price Ranges for Wood Adhesives
Table 2	U.S. Consumption of Natural and Synthetic Adhesives
Table 3	North American Waferboard Industry
Table 4	Average Variable Costs for Representative North American Waferboard, OSB and Plywood Mills in 1986
Table 5	Typical Canadian Plywood Glue Mix
Table 6	Variables in Plywood Bonding
Table 7	Typical Powdered PF Properties
Table 8	Comparison of Adhesive Usage in Consolidating One Cubic Foot of Various Wood Elements of Douglas-fir, Original Density 28 lbs/cubic foot
Table 9	Range of Application Parameters for Adhesives in Specific Wood Products
Table 10	Chemical Characteristics for a Number of Lignin Materials
Table 11	Molecular Weight Averages and Molecular Weight Ranges for Synthetic and Lignin Polymers
Table 12	Softening/Glass Transition Temperatures of PF and Lignin Adhesives
Table 13	Effect of Lignin Cost of PF-lignin Adhesive Cost at Three Substitution Levels

LIST OF FIGURES

Figure 1 Comparison Between Schematic Chemical Structure of Lignin and PF resin

Figure 2 Partial Mechanism of Oxidative Cross-linking of Lignosulfonates

Figure 3 Representative Reactions That Can Occur Between Lignin and Formaldehyde in Alkaline Solutions

Figure 4 Common Aromatic Unit Structures Present in Lignin

1.0 INTRODUCTION

Lignin is a polyaromatic substance commonly present in most plant cell walls. Approximately 18 to 33 percent of the weight of wood consists of lignin. The abundance of this resource throughout the world and its renewable nature has made lignin attractive as a potential source of chemicals. With the certainty that present petrochemical sources are of a finite nature, lignin can be viewed as an important future source of aromatic chemicals.

Present commercial lignin isolation methods are directly related to the pulp and paper industries where two major pulping methods are used (Sarakanen and Ludwig, 1971). The older sulfite process yields lignosulfonates which are utilized commercially to a limited extent, burned or disposed of as a waste product. The newer kraft process uses alkaline sodium hydroxide and sulfide as pulping chemicals to achieve lignin separation from cellulose. This lignin is primarily burned and used as an energy source for recovery of pulping chemicals. In Canada, annual lignin production is about 1.5 to 2.0 million metric tonnes with the majority being kraft lignin (Anonymous 1985b). Only a very minor portion of these are utilized as chemicals. Placing a value on crude lignin depends upon the exact industrial purpose for which this material will be used. As an energy source value as low as 12¢ per kilogram for lignosulfonates and as high as about 44¢ per kilogram for kraft lignins have been calculated (Chum et al., 1985).

Recent interest in the conversion of lignocellulosic biomass into liquid fuels and chemicals through enzymatic hydrolysis reactions has led to new bioconversion processes such as steam explosion and organosolv pulping. These milder processes often are designed to yield concentrated, fermentable sugar solutions, free of lignin. Projections are that a considerable amount of these materials will be produced in the near future (Chum et al., 1985). The lignins isolated from these processes contain few inorganic materials and tend to be more soluble in organic and aqueous-alkaline solvents than conventional pulping lignins. Economic considerations make it desirable that bioconversion involve an integrated process whereby the lignin component is utilized as a highly valued product.

The potential for lignin chemical utilization has been viewed in a highly optimistic manner for a number of years. Reality has shown that only a very limited amount of lignin presently has found its way into product applications. These lignins have been utilized either in their crude isolated form or further fractionated and refined through chemical conversion to a more purified product. The primary markets for lignin products (Lin, 1983) have been in:

1. Industrial surfactants where they are utilized for dust control, dye and pigment dispersants, animal feed pelletization, concrete additive and oil drilling mud additive. Large new markets for

lignin surfactant are anticipated in enhanced oil recovery and coal slurry transportation;

2. Asphalts where lignins are used as extenders;

3. Carbon black substitution as a reinforcement agent for rubber;

4. Adhesive substitution for either wood bonding or as molding compounds;

5. Lignin plastics where they could be used to partially substitute phenolic and urea-based resins, polyurethanes and epoxy products;

6. Controlled release agents where they are biologically compatible with the environment and function to allow the slow release of biologically active agents; and

7. Low molecular weight chemicals, where phenolic monomers and some alcohols can be recovered.

Increased market acceptance for lignin products will require a sustained effort to overcome some of the present process limitations of these materials. These limitations relate to the complex nature of lignins, their inhomogeneity, their lower reactivity and limited solubility in many solvents. These issues will be addressed further in some of the latter sections.

The purpose of this report is to focus on the use of lignins as wood adhesives, specifically to provide a perspective on the potential of enzymatic lignin-based adhesives.

Due to both structural and chemical similarities much attention has been directed to using lignin as a substitute for phenol-formaldehyde (PF) resin (Campbell and Walsh, 1985). The impetus for this approach has been the linkage between petroleum and phenol prices and the severe impact the oil crisis of the 1970's had on wood adhesive costs. Both the realization that almost 50 percent of PF resin production is utilized in wood products and the inevitable prospect of a return to high oil costs will result in a continual desire to substitute phenol with lower cost lignin adhesives (Anon., 1984).

In Canada, PF resin consumption in wood products is about 35 million kg. (based on 100 percent resin solids) annually (Anon., 1984). The North American market is about eight times greater. Similar volumes of urea formaldehyde (UF) resins also are utilized. The economics of using lignin as a replacement for PF adhesives will depend upon its relative cost and bonding efficiency. Table 1 gives current prices for commodity adhesives used in the wood industry (Anon., 1986). Apart from UF adhesives, crude lignin prices from pulping operations are significantly lower than these costs. Any processing costs incurred to improve the applicability of lignin as an adhesive substitute can rapidly increase the market costs of these materials.

Table 1

Current Price Ranges for Wood Adhesives

Adhesive	Price per Ply
PF (100% liquid)	$1.00 - $1.20
PF (powder)	$1.30 - $1.60
UF (100% liquid)	$0.45 - $0.50
PRF (100% liquid)	$4.50 - $6.00

The purpose of this report is to focus on the use of lignins as wood adhesives, giving an overview of the many approaches used to utilize pulp in lignins as adhesives and to provide a perspective on the potential for enzymatic lignin-based adhesives as produced through steam explosion or organosolv processes. To accomplish this, the report is divided into three segments. The first covers the historical development of adhesives based on spent sulphite lignins and the present status of such lignin adhesives. Some reference to recent bonding work with biomass lignin is also considered. The second part discusses application and property requirements of adhesives needed for the production of various wood composites. These requirements are compared with physical and chemical properties of presently available lignins. The third section presents some future prospects for lignins in relation to newer technology and research areas where further activities would be beneficial. The primary focus of these discussions will be directed towards enzymatic lignin adhesives.

2.0 STAFF TEAM

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3.0 PART I

AN OVERVIEW OF THE USE OF VARIOUS LIGNINS IN ADHESIVES FOR WOOD COMPOSITES

3.1 INTRODUCTION

The success of the modern reconstituted wood products industry is largely due to the development of high quality synthetic adhesives as replacements for lower quality natural adhesive such as fish, blood or protein glues (Table 2). It also reflects our ability to adapt to a lower quality forest resource. Wood composites randomize the defects of wood and permit the production of large dimension panels or lumber of high quality from lower quality trees. Through the years, wood composites have gained recognition and it is expected that this trend will continue into the future. A good indication of this is illustrated by the exponential expansion of the waferboard sector in North America (Table 3).

Today, the wood composite panel industry depends almost exclusively on petroleum-based synthetic resins such as urea-formaldehyde, melamine-formaldehyde and phenol-formaldehyde. Since these are derived from oil (phenolic resin) and natural gas (amino resin), the availability and price of synthetic resin are tied directly to oil and natural gas. The oil embargo of 1974 followed by the energy crisis have demonstrated the danger of relying entirely on the non-renewable petroleum sources. Even today when the supply of petroleum seems to momentarily surpass the demand, the cost of synthetic resin adhesives still remains as a significant portion of the manufacturing cost of reconstituted wood products. For example, recent estimates and projections for the Canadian Waferboard/OSB industry indicated that in 1986, the glue component comprised 14% of the total variable costs (TVC) of manufacture. Comparable figures for U.S. waferboard revealed the glue component to be an average of 18% of TVC in 1986 (Table 4). High costs and potential shortages of petroleum resources have stressed the importance of developing reliable but less expensive adhesives, based on a readily available natural resource. A significant reduction in glue costs would confer a competitive advantage to manufacturers who capitalize on cost reductions. For example, considering the 8.013 billion sq. ft. consumption of 3/8 inch waferboard/OSB shown in Table 3, it may be calculated that a reduction of glue costs in the neighbourhood of $5 (U.S.)/thousand sq. ft. for all producers would translate into a net saving of at least $40 million (U.S.) (Howatson, 1986).

Parallel to the developmental work on synthetic resins, extensive research has been conducted in an effort to formulate quality adhesives based on non-petroleum resources. Lignin, the natural binder of wood was identified as one of the most promising substrates for this application. It is the most abundant renewable resource on earth next to carbohydrates (cellulose, hemicellulose). It has many desirable features such as: it is domestically available in large quantities at a low cost and it has a phenyl-propane repeating unit very similar to phenol-formaldehyde (Figure 1). For these reasons, a

Table 2

U.S. Consumption of Natural and Synthetic Adhesives

	1971		1979		1985	
	billion lb	%	billion lb	%	billion lb	%
Natural	1.25	45	1.2	30	1.3	24
Synthetic	1.55	55	2.8	70	4.2	76
Total	2.8	100	4.0	100	5.5	100

Source: Hagler, Bailly & Company. 1986.

Table 3

North American Waferboard Industry
(annual capacity MSF, 3/8 INCH BASIS)

	1979	1982	1986*
CANADA	885(6)	1605(11)	2615(15)
USA	285(2)	1810(8)	5398(32)

* Includes mills in place and mills announced or under construction.

Table 4

Average Variable Costs for Representative North American Waferboard[1], OSB[2] and Plywood Mills in 1986 (Cdn.$/MSF, 3/8 inch Basis)

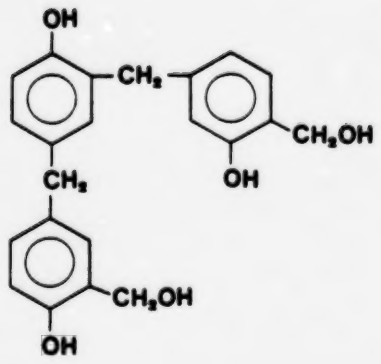
	WAFERBOARD	OSB	PLYWOOD
WOOD (delivered)	44.72	49.36	90
LABOR	21.63	18.21	69
ENERGY	5.01	7.60	13
GLUE	15.74	23.03	14
WAX	5.31	3.93	--
MISC	17.96	19.33	29
RESIDUE INCOME	--	--	--
GENERAL AND ADMINISTRATIVE	5.52	6.07	16
TOTAL VARIABLE COSTS	115.87	127.53	202

1 Average variable costs for Ontario and Quebec Waferboards Mills.

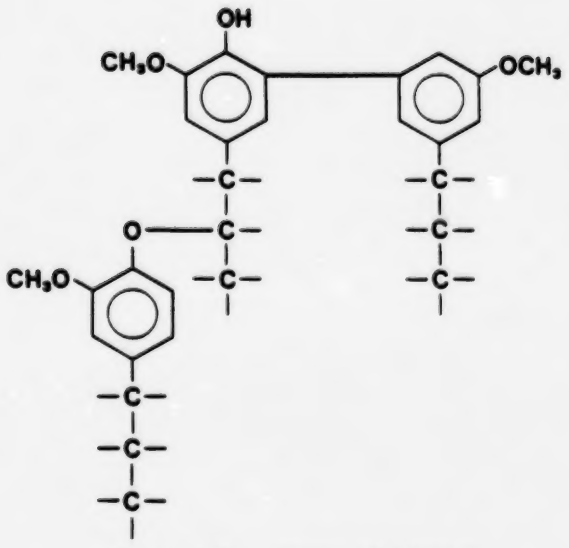
2 Average Variable costs for U.S. South OSB.

3 Average Variable costs for B.C. Plywood Mills

Source: RESOURCE INFORMATION SYSTEMS, INC. 1986.



Partial Structure of PF
before Curing



Partial Structure of Lignin

Figure 1. Comparison between schematic chemical structure of lignin andPF resin.

tremendous amount of work has been expended to utilize lignin from pulp and paper mill residues as a replacement for synthetic resins, primarily phenol-formaldehyde resins.

The main obstacle to overcome in the conversion of pulp and paper lignin to useful adhesives is low reactivity. During the last 30 years, a tremendous amount of work was conducted to improve the reactivity of lignin and to formulate adhesives. With the arrival of new technology such as ultrafiltration and a better knowledge of lignin structures, some success in formulating lignin adhesives has been achieved. At Forintek for example, several successful trials were conducted using kraft and sulfite lignins as a partial replacement of phenolic resins in waferboards. In fact small amounts of kraft and sulfite lignin are presently being used commercially as adhesive extenders for particleboard and plywood Changes in waferboard/OSB standards will soon permit lignin based adhesives to be used in waferboard and OSB panels. However due to its lack of reactivity to date, lignin has been limited to a role of resin filler or extender.

It is known that the reactivity of lignin could be improved through chemical treatments such as demethylation or oxidation. However, these can be expensive operations and most lignin modifications result in products which may not compete with the present cost of synthetic resins. One more feasible approach could be to conduct chemical treatments directly during the pulping process, however, the well-established wood pulp industry to date has expressed little interest in the commercialization of lignin adhesives. During the sulfite or soda process, wood is cooked under very rigid schemes in order to produce high quality paper. Lignin is the non-desirable product which must be solubilized and removed with other waste chemicals without any considerations towards its quality or uniformity. Future advancements in wood pulping methods may lead to economically viable processes whereby not only pulp but valuable, reactive, lignin products would be recoverable. Contrary to the approach of the present pulping industry, utilization of the steam explosion lignin is essential for the economic viability of the whole bioconversion process.

With consideration being given to the production of liquid fuel by the steam explosion of cellulosic feedstock, a large quantity of lignin may be produced. It may thus be possible to optimize the steam explosion process in order to produce high quality fuel and generate reactive lignin substrates.

In this part of the report, an overview of published reports on various types of lignins in adhesive formulations over the past 20 years has been documented. The review is divided in three sections. Section A deals with lignin-based wood adhesives not in combination with UF or PF. It includes the use of modified or unmodified lignosulfonate and kraft lignins mixed with furan resins and the use of epoxidized lignin. Adhesives where the lignin is cross-linked by means of radical coupling are included in this section. Examples of chemical bonding of wood through a free radical graft polymerization

mechanism has also been included. Sections B deals with lignin-based wood adhesives in combination with UF, PF, or Isocyanates and includes lignosulfonates, organosolv and kraft lignins.

Section C deals with bioconversion lignins, i.e. lignin extracted with dilute alkali or ethanol from steam-exploded wood; the by-product lignins from the enzymatic treatment of the steam-exploded wood; and the residual lignin from the acid hydrolysis of wood chips.

Emphasis has been placed on adhesives used in particleboard, waferboard and plywood manufacture.

3.2 SECTION A. LIGNIN-BASED WOOD ADHESIVES WITHOUT COMBINATION WITH UF OR PF

3.2.1 Comments on Section A

There have been many attempts to use sulfite or kraft liquor directly as a wood adhesive without extensive use of resin copolymers. In 1963, a process was developed (Pederson process, abstracts 1 and 4) in which wood chips were simply mixed with 20 to 25% of their weight of a 50% technical spent sulfite liquor (SSL) pre-adjusted at pH 3.0 with acetic acid. The coated wood chips were pressed at 185°C for 30 min and post heated at 195°c for 80 min in an autoclave. The resultant boards were found to have strength properties similar to UF or PF bonded panels with good dimensional stability and surface quality. The process has been applied in mill scale tests, but development was discontinued because of the high energy costs involved in the two-stage heating treatment. In 1973, a variation on this process was proposed by Shen (abstracts 5 and 19) who used sulphuric acid as an acid catalyst for SSL, to produce a binder for exterior waferboard. Press cycles of 5 minutes for 7/16 inch (11 mm) thick panels (press temperature of 210°C) were possible with the acidified SSL resin. The main attraction of this process was in cost savings. However possible problems associated with the use of strong acid catalysts have prevented practical application of the system. It was later discovered by Shen, Calvé and Fung, that ammonium based spent sulfite liquor (NH_4SSL) could be used directly as an adhesive without addition of any acid catalyst (abstract 20). Long press cycles or high press temperature were however required to cure the NH_4SSL adhesive. The press cycle for 7/16 inch (11 mm) thick waferboard was reduced to 6 minutes at 410°F (210°C) press temperature by using the lower molecular weight fraction of NH_4SSL containing a high proportion of carbohydrates. It was demonstrated that both the lignin and the carbohydrates present in NH_4SSL contributed to the bonding process (24).

With today's fast curing phenolic resins, press cycles of 3 to 4 minutes are possible. This represents a 100 percent greater plant production capacity if compared to the 5-6 minutes press cycle of first generation PF resins, acidified SSL or low molecular weight NH_4SSL. The low cost advantage of using inexpensive lignin adhesive is offset by lower plant production capacity if the lignin is slow curing and requires a longer press cycle. These adhesives have found no practical application yet.

An interesting approach which avoids the high energy requirements of previous processes, was proposed by Nimz et al (abstracts 6, 7 and 18). It involves the cross-linking of the lignin molecules by radical coupling instead of condensation reactions (see Figure 2). The curing agent is hydrogen peroxide. Sulphur dioxide is used as a catalyst. This procedure claims a number of advantages: less energy is required and the use of mineral acid is avoided. There are no corrosion problems. Due to the exothermic reaction, the homogenity of the board is expected to be better; charring is avoided and thicker boards can

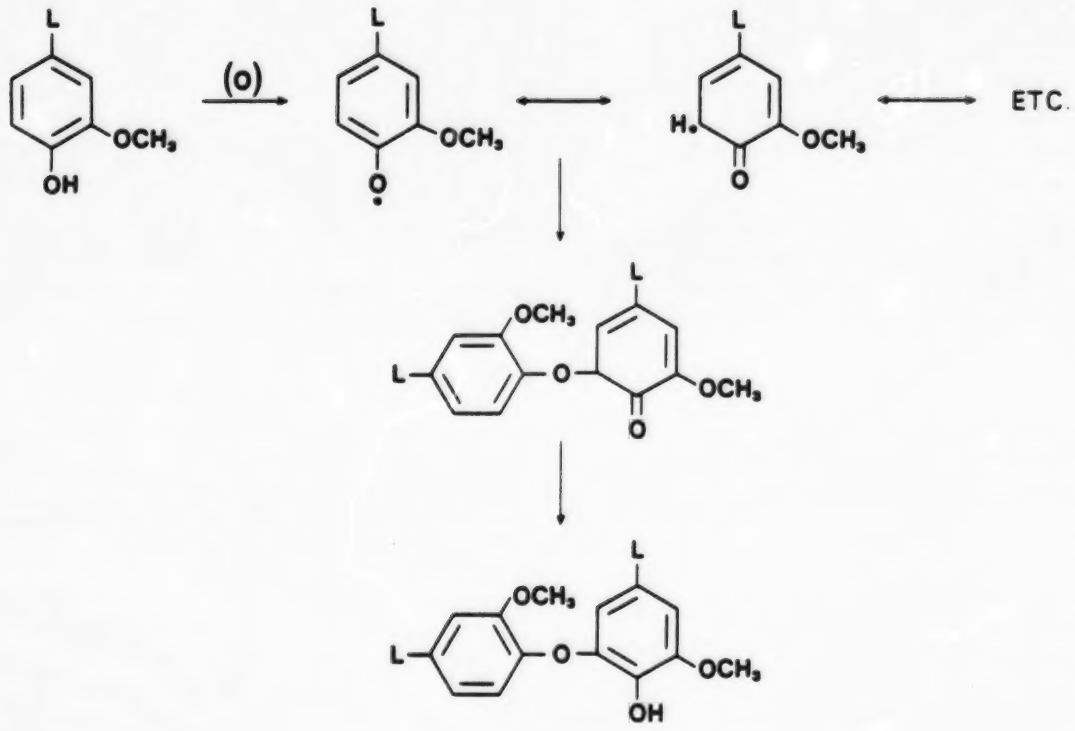


Figure 2. Partial mechanism of oxidative cross-linking of lignosulfonates.

Source: See abstract 27.

be pressed in shorter pressing times when compared with UF boards; no formaldehyde is released. At the present time, this procedure may be used for the production of medium-density interior grade particleboard bonded with 20% SSL, (dry weight basis), at pressing temperatures between 100 and 120°C. It has found no application yet because of the cost of the hydrogen peroxide required. It is hoped that the process may be further improved to meet exterior grade standards for particleboards.

Other nonconventional bonding methods involve the treatment of wood surfaces with oxidizing agents such as hydrogen peroxide, nitric acid, peroxyacetic acid, potassium ferricyanide or sodium dichromate and polymerizing (or gap filling) materials such as furfuryl alcohol, ammonium SSL with furfuryl alcohol, formaldehyde or maleic anhydride (abstracts 7,11,12,23,25). These techniques involve graft polymerization to induce bonding in wood composites. It is possible to obtain a panel with acceptable mechanical properties and water resistance using these techniques; however, the processes may not be economically viable until less expensive chemicals can be identified. For example as reported by Zavarin (abstract 27) the Philippou process would be more expensive than phenol-formaldehyde: "In December 1981, the cost of binder raw materials for 100 ft^2 of HNO_3 was estimated to run $22.60, vs. $28.30 for H_2O_2 board, and $21.00 for phenol-formaldehyde board".

Recently, (Krzysik and Young, 1986) it was claimed possible to generate dry and wet wood bond strengths equivalent to phenol-formaldehyde bonded samples, when methylolated lignin was used in combination with 3N sodium hydroxide for activation. Press cycles of 30 minutes were used for 5/16 inch (7.9 mm) thick panels pressed at 302°F (150°C). This development is still at the experimental stage.

Lignin may also be modified for the production of epoxy type adhesives. Since epoxy resin is more expensive than phenol-formaldehyde, this leaves more place for an economically viable chemical modification of lignin. For example, lignin may be esterified with butanol and then reacted with epichlorohydrin (abstracts 8 and 10). At this time, little work with epoxy lignins has been reported.

3.2.2 Section A Literature Review

1 - Pedersen, A.H.F.; Jul-Rasmussen, J. 1966. Manufacture of chipboard and the like. Canadian Pat. 743,861.

A method is described for using spent sulfite liquor for particleboard in which the spent liquor is adjusted with acetic acid to a pH of about 3. In order to obtain a satisfactory bond, two stages of curing the binder are stated as being essential. The first step comprises pressing a 1/2 inch (0.127 mm) board at 185°C (365°F) for 30 minutes. In the second step, the board is placed in an autoclave and heated to 195°C (385°F) for 80 minutes under pressure.

2 - Holzer, T., Wust, H.V. 1966. Fr. Pat. 1,438,765. Preparation of water-soluble condensation products from protein materials and lignosulfonic acids (LSA).

Protein materials, such as animal hide hydrolyzate, bone glue, casein, gelatin, blood, or soybean protein, are reacted with LSA with heating at a pH above the isoelectric point of the protein material. The water-soluble product of the reaction are used as adhesives for paper, board and other fibrous webs.

3 - Niilo-Rama, J.E.; Smiley, R.J. 1969. Treatment of spent sulfite liquor. Can. Pat. 825,155.

SSL is heated with an aromatic diamino compound and then cooled to permit recovery of a lignosulfonic acid derivative of the diamino compound as a precipitate. Carbohydrates and the pulping liquor base can be separately recovered from the precipitate. The lignosulfonic acid compound is of use in making particleboards, binders and other products. The diamino compounds used, for example, can be prepared by the reaction of aniline, acetone, dicyandiamide and HCl in alcohol.

4 - Johanson, T.A. 1971. Particleboard bonded with sulfite liquor. Proceedings of the fifth Washington State University Symposium, Pullman, Washington, June 1971, pp. 11-21.

Board prepared with spent sulfite liquor (SSL) adhesive according to the Danish process (abstract[1]) were tested over a period of 6 years by several European institutes. The dark brownish SSL board were found to possess lower moisture absorbency and swelling tendencies than boards bonded with thermosetting resins.

5 - Shen, K.C. 1974. Modified powdered spent sulfite liquor as binder for exterior waferboard. For. Prod. J. 24 (2): 38-44.

Medium density aspen waferboard bonded with 4-5 percent SSL and less than 1 percent sulfuric acid was produced with the same press time and physical properties as those found in commercial phenolic-bonded waferboard at a potential saving of 25 percent in material cost. The wafers first were sprayed with acid and then mixed with spray-dried SSL. Panels of 3/8 inch (9.5 mm), containing 5 percent SSL and 1.2 percent acid, retained 35 percent of the dry bending strength when pressed 4.0 minutes at 410°F (210°C).

6 - Nimz, H.H.; Razvi, A.; Mogharab, I.; Clad, W. 1974. Binder or adhesive for manufacturing wood-based materials as well as for gluing materials of various types. German Pat. 2,221,353.

The binder or adhesive, for use in the manufacture of particleboard or in gluing wood or plastic materials is produced by mixing shortly before use, SSL or kraft liquor, a redox

component (e.g., potassium ferricyanide) and an oxidizing agent (e.g. hydrogen peroxide). The composition hardens as a result of radical cross-linking due to oxidative coupling of the lignin components in the spent pulping liquor.

7 - Nimz, H.H.; Mogharab, I.; Gurang, I. 1975. Oxidative coupling of spent sulfite liquor. Proc. 8th Cellulose Conference, Syracuse. (3):1225-30.

Cross-linking of SSL by oxidative coupling to a cation-exchange resin is reviewed. In addition, the cross-linking of SSL by ten different polyfunctional compounds was investigated. Highest resin yields were obtained with epichlorohydrin and polyethyleneimine/tris (chlorethyl) ammonium hydrochloride.

8 - D'Alelio, G.F. 1975. Polymerizable lignin derivatives. U.S. Pat. 3,905,926.

Acidic groups of lignin are esterified with butanol, the product is reacted with epichlorohydrin in the presence of a base. After using a curing agent (i.e. metaphenylenediamine) the derivative is used as a thermosetting composition.

9 - Chow, S. 1975. Bark Boards without Synthetic Resins. For. Prod. J. 25(11); 32-37.

A method of making bark boards using bark particles without adhesives is reported. The polymerization of the phenolic extractives and lignin in bark are possibly responsible for the adhesion. Pressing temperatures in the range from 250°C (482°F) to 300°C (572°F) were found most effective in reducing press times for bark boards to those for comparable waferboard or plywood manufacture.

10 - D'Alielo, G.E. 1976. Polymerizable lignin derivatives. U.S. Pat. 3,984,363.

Lignin (sulfonates or alkali lignins such as kraft lignin) is first subjected to esterification of phenolic hydroxyl and of carboxl groups and is then reacted with an epoxidizing agent such as epichlorohydrin. A number of compounds may be used as curing agents such as: diethylenetriamine, phthalic anhydride and others. For most applications, however, only the phenolic hydroxyls are converted to oxirane (epoxide) groups, leaving the carboxyls and hydroxyls unchanged or unesterified.

11 - Philippou, J.L. 1977. Chemical bonding of wood. Univ. California (Berkeley). Ph.D. thesis. 1977. 232 p. Univ. Microfilms, Ann Arbor, MI 48106.

Medium density particleboards with strength and water resistance properties superior to conventional PF-bonded particleboards were prepared by treating the wood surfaces with oxidants (viz., hydrogen peroxide, peroxyacetic acid, nitric acid, or potassium

ferricyanide) and polymerizing materials (viz., furfuryl alcohol; ammonium SSL with furfuryl alcohol, formaldehyde, maleic anhydride, or phenol with furfuryl alcohol). Strong and water-resistant bonding comparable to that of phenolic adhesives developed also in plywood and other laminated panels. The strength and water durability of the bonding depends on the amounts of chemicals, the pressing conditions, the density of the products, and the species of wood. Results show that furfuryl alcohol and ammonium SSL in the presence of oxidants, graft onto wood particles. Differential scanning calorimetry thermograms, IR and UV absorption spectra provide evidence of chemical bond formation between wood and polymerizing chemicals. The results point out that the bonding process involves a free radical graft polymerization mechanism.

12 - Johns, W.E.; Layton, H.D.; Nguyen, T.; Woo, J.K. 1978. Nonconventional bonding of white fir flakeboard using nitric acid. Holzforschung 32 (5): 162-166.

Techniques for the nonconventional bonding of wood which attempts to induce chemical changes at the surface of the wood, are briefly reviewed. The properties of flakeboards manufactured by treating white fir (Abies concolor) flakes, first with nitric acid followed by an aqueous mixture of ammonium lignosulfonate, furfuryl alcohol and maleic acid, are discussed. Comparisons with phenol-formaldehyde bonded control boards show that the nonconventional bonding techniques yielded boards with higher modulus elasticity and lower thickness swelling and water absorption, while the phenolic bonded boards had higher bending strength and tensile strength. Effects of nitric acid concentration, application rate, assembly time, pot life of cross-linking mixture and total assembly time on the physical properties of the nonconventionally bonded panels are discussed.

13 - Bornstein, L.F. 1978. Lignin-based composition board binder comprising a copolymer of a lignosulfonate, melamine and an aldehyde. U.S. Pat 4,130,515. To: Georgia Pacific Corp.

Polymerization of sodium-lignosulfonate with formaldehyde and melamine in the presence of sodium hydroxide gave a methylolated resin adhesive for use in the manufacture of particleboard. Southern pine chips treated with 7-9 percent resin, 1 percent wax, pressed 4 minutes at 300°F (149°C) and 500 psi (3.44 MPa) at 53 lb/ft^3 (849 kg/m^3) density produced panels with good mechanical properties and low thickness swelling.

14 - Svenska Traeforskningsinstitutet 1979. Synthetic resins from paper mill wastes. Belg. Pat. 874,584. Ca 91:A1 58546.

Lignin-containing resins, useful as particleboard binders and similar adhesives are obtained by treating spent pulping liquors containing sugars and lignin so as to convert the sugars to furfural derivatives, adding lignin if necessary and condensing

the lignin with furfural derivatives. Thus, 15 percent Ca-base SSL is acidified to pH 0.3 with sulfuric acid, heated 30 minutes at 90°C, filtered to remove Ca sulfate, evaporated to 55 percent solids content, and adjusted to pH 1.0. Wood particles coated with 10 percent of this solution (based on dry solids) are pressed 5 minutes at 180°C and 2 MPa to give boards of acceptable quality.

15 - Kubin, J.; Rajkovic, E.; Hespodarik, A. 1979. Particleboard. Czech. Pat. 179,158. CA: 92:A43547

A mixture of spent sulfite liquor (solids content over 30 percent), carbamide, paraffin, and ammonium chloride is used as a binder for particleboard manufactured by pressing the mixture with fir chips at 150°C.

16 - Holmquist, H.W. 1980. Preparation of a lignocellulosic (LC) composite. U.S. Pat. 4,186,242. To: Georgia-Pacific Corp.

In the manufacture of composite materials such as particleboard, hardboard, or plywood, using a UF adhesive and a pressing step, the release of formaldehyde during and after manufacture of the product is reduced by the treating the materials being used with ammonium LS (e.g., in the form of ammonium-base SSL) prior to the pressing step.

17 - Polovinkin, V.L.; Grin, V.N.; Milovidov, A.S. 1980. Method for producing an adhesive for gluing fibrous materials. USSR pat. 730,992. CA 93: A 74267.

Adhesive strength is improved, gluesetting time is shortened, and tack is increased in an adhesive produced by treating ammonium-base SSL (from the pulping of wood) with Ca hydroxide or oxide if 2-5% (of the dry weight of SSL) of alum or Al oxide is added at pH 8-11 and 40-80°C.

18 - Nimz, H.H.; Hitze, G. 1980. The application of SSL as an adhesive for particleboard. Cellul. Chem. Technol. 14(3): 371-382.

Spent sulfite liquor (SSL) is extensively cross-linked by oxidative coupling with hydrogen peroxide in the presence of sulfur dioxide. The strongly exothermic reaction, which leads to an insoluble resin, allows the application of SSL as an adhesive for particleboards. In comparison with conventional particleboards, made with urea-formaldehyde adhesive, no release of formaldehyde occurs from SSL particleboards. Further advantages are: low press temperatures (120°C), no wax sizing, better homogenity of the boards and the manufacture of thicker boards at short press times. The pH of the glue mix is 2 without 'hardener', but with ammonium chloride as 'hardener' a pH of 4.5 leads to particleboards with similar properties as boards obtained at pH 2. The results apply to calcium base SSL pretreated by fermentation to alcohol.

19 - Shen, K.C. 1980. Binding Lignocellulosic Materials. U.S. Patent 4,193,814.

This patent granted in 1980 relates to the process previously described by Shen in 1974 (abstract 5). Calcium, ammonium, magnesium or sodium based spent sulfite liquor (SSL) treated with sufficient sulfuric acid to provide a lignosulfonic acid content of not less than 0.8 milliequivalent weights of NaOH per gram of SSL solid, make it possible to produce particleboards with press times and physical properties comparable to phenol bonded boards but at considerably reduced material cost.

20 - Shen, K.C.; Fung, D.P.C.; Calvé, L. 1981. Method of Binding Lignocellulosic Materials. U.S. Pat. 4,265,846.

A low cost method of binding lignocellulosic materials utilizing ammonium based spent sulfite liquor (NH_4SSL) alone as binder is described. No acidification of NH_4SSL prior to bonding is required to produce a boil-proof bond if a higher curing temperature is employed. The low molecular fraction containing a higher portion of reducing sugars has a better bonding quality and faster curing rate.

21 - Holsopple, D.B.; et al. 1981. Epoxide-lignin resins. U.S. Pat. 4,265,809. May 5, 1981. CA:95(6)45045w.

Epoxidation of kraft lignin-mesityl oxide-formaldehyde reaction product with hydrogen peroxide or sodium peroxide gave an epoxide-lignin resin for use in the manufacture of adhesives and plastics.

22 - Leitheiser, R.H; Bogner, B.R. 1982. A water-diluted furan resin binder for particleboard. J. Adhes. 14, (3-4): 305-13.

A water-dilutable furan resin made from agricultural residues can be used as a binder for particleboard. Board properties were comparable to those of commercial phenolic binders. Board costs can be significantly reduced by using low cost ammonium lignosulfonate as a resin extender and catalyst. A resin level of 7 percent by weight of oven-dried wood was used, with a press temperature of 350°F (177°C), a press closing cycle of one minute and a press time of 7 minutes.

23 - Philippou, J.L.; Johns, W.E.; Nguyen, T. 1982. Bonding wood by graft polymerization: Effect of hydrogen peroxide concentration on the bonding and properties of particleboard. Holzforschung 36(1):37-42.

Particleboards from white fir (Abies concolor), Douglas fir (Pseudotsuga menziesii), and Bishop pine (Pinus muricata) were bonded by graft polymerization using hydrogen peroxide as a surface activator. Polymerization cross-linking agents were furfuryl alcohol and mixtures of ammonium lignosulfonate with furfuryl alcohol or formaldehyde. The strength and water

resistance of the boards were suitable for exterior structures. Properties were improved by increasing the amount of hydrogen peroxide. Differences due to wood species are discussed.

24 - Calvé, D.; Fréchet, J.M.J. 1983. Wood Adhesives Based on Lignin Wastes: Influence of the Carbohydrates in the Polymerization of Spent Sulfite Liquor. J. Applied Polym. Sci., 28:1969-1980.

The influence of carbohydrates on the thermosetting properties of ammonium spent sulfite liquor (NH_4SSL) was studied using various fractions of the liquor obtained by ultrafiltration. While low molecular weight carbohydrate-rich fractions thermoset readily, higher molecular weight sugar-free fractions failed to thermoset. Optimum results with wood particles were obtained by adjusting the carbohydrate to lignin ratio.

25 - Brink, D.L.; Kuo, M.L.; Johns, W.E.; Birnbach, M.J.; Layton, H.D.; Nguyen, T.; Breiner, T. 1983. Exterior particleboard bonded with oxidative pretreatment and cross-linking agent. Holzforschung 37, (2): 69-78.

A four-stage process for bonding wood flakes to form particleboard is described. Flakes are first pretreated with an oxidant (nitric acid or hydrogen peroxide). A cross-linking agent is then prepared by adding an aqueous solution of maleic acid to a solution containing furfuryl alcohol and ammonium lignosulfonate. The mixture is then added to the pretreated flakes, the material assembled and pressed. The major parameters controlling the reactions are discussed. Boards meeting exterior grade specifications were produced only from nitric acid-treated flakes. Optimum board making parameters at 180°C (356°F) press temperature, 7 minutes press time and 9.5% mat moisture content were established for 12.8 mm (0.5 inch) thick panel.

26 - Haars, A; Huttermann, A. 1984. Process for producing a binder for wood materials. U.S. Pat. 4,432,921.

A process is described by which phenolic substances such as lignosulfonates are oxidatively polymerized (radical coupling) with enzymes. The phenolic material then becomes an active binder and can be applied to wood particles. White-rot fungi, such as Formes Annosus (among others) are used as the source of phenol-oxidizing enzymes. The boards may be pressed at room temperature.

27 - Zavarin, E. 1984. "Activation of Wood surface and nonconventional bonding" in the chemistry of solid wood, advances in chemistry series 207, Rowell, R.M. Eds., American Chemical Society, Washington D.C. pp 349-400.

A review on activation of wood surface and nonconventional bonding citing to 215 references.

28 - Pantyukov, V.P.; El'bert, A.A. 1985. Adhesive capacity of lignosulfonates. Leningrad Lesotekh. Aka. (2), 69-71. CA:103,7925j, 1985.

Of the four lignosulfonate binders for particleboard studied, NH_4SSL was the most promising. Optimum molding conditions for particleboard using that binder were: molding time: 1 min./mm, molding temp.: 195°C, pH of NH_4SSL:08. The boards had compressive strength of 15-17 MPa and a swelling of 8-15%.

29 - Young, R.A.; Fujita, M.; River, B.H. 1985. New approaches to wood bonding a base-activated lignin adhesive system. Wood Sci. Technol. 19:363-381.

It was found that aqueous sodium hydroxide can effectively activate wood surfaces to give strong dry autoadhesive bonds, but only low wet strength were obtained. However, excellent dry and wet wood bond strengths, equivalent to phenol-formaldehyde bonded samples, were obtained when methylolated lignin was used in combination with 3N sodium hydroxide activation.

30 - El'bert, A.A.; Dorokhova, O.V.; Khotilovich et al. 1985. Study of the properties of modified lignosulfonates as binders for fiberboard. (Leningrad Lesotekn. Akad). Khim. Drev. (5):61-5. CA:104,35475, 1986.

Replacing Na^+ with Al^{3+} in lignosulfonates (I) resulted in an increase of their relative dynamic viscosity as well as a decrease of the velocity of electrophoresis and surface tension. Heat treatment of (I) was accompanied by partial cross-linking. (I) can be used as a binder in fiberboard manufacture.

3.3 SECTION B. LIGNIN-BASED WOOD ADHESIVES IN COMBINATION WITH UREA-FORMALDEHYDE (UF) OR PHENOL-FORMALDEHYDE (PF)

3.3.1 Comments on Section B

As indicated in section A, lignin alone can not replace UF or PF resin binders for wood composites unless expensive oxidizing agents or long press cycles are used. An alternative is the partial replacement of UF or PF resins with lignin. This is the area of research where the greatest amount of time and energy has been spent, as evidenced by the number of patents and journal articles on the subject.

Referring to partial substitution of phenolic resin with lignin, in 1971, Roffael and Rauch (abstract 32) demonstrated that the rate of cure of SSL adhesive could be accelerated by addition of ä novolak type phenolic resin copolymer. The press cycles were shortened to 5-7 minutes with pressing temperatures of 428 to 482°F (220 to 250°C). Shorter press cycles were reported when SSL was used as an extender for alkaline curing phenolic resole (abstracts 33, 34 and 35). The process was later improved by Forss and Furhmann in 1975-79 (abstracts 37 and 49). Their work involved the isolation of a high molecular weight lignin by ultrafiltration from either spent sulfite or alkali pulping liquors and copolymerization with PF resins (Karatex adhesive). A typical Karatex adhesive mix was claimed to replace 36% of the resin in the finished adhesive formulation. This process has been used commercially for a short period of time but the production of Karatex resin was not pursued, apparently because of the slow curing properties in comparison to existing commercial phenolic resins.

The limited reactivity of kraft lignin can be increased by methylolation with formaldehyde (abstract 38). In 1978, Clarke and Dolenko (abstract 45) reported a process where methylolated kraft lignin was used in combination with an acid curing phenolic resin for the manufacture of waferboard and plywood. At 70 percent PF replacement 7/16 inch (11.1 mm) thick waferboards of exterior quality are produced using a press cycle of 5 minutes at 400°F (204°C) . The process was evaluated successfully at a mill trial. As press cycles of 3 to 4 minutes are being used commercially for the production of 7/16 inch (11.1 mm) thick waferboard an acceptable lignin based adhesive must be competitive with these press cycles.

At the Eastern Laboratory of Forintek a faster curing kraft and sulfite lignin based adhesive was recently developed (abstracts 57, 58 and 74). The adhesive system consists of a mildly acidic lignin-phenolic resin dispersion. The resin adhesive may be applied as a liquid or powder. An acid catalyzed- alkaline based phenolic resin was used as an active copolymer for methylolated kraft lignin or ammonium based spent sulfite liquor. A large part of the success of this process can be attributed to the proper choice of the phenolic resin copolymer which consists of a mixture of high and low molecular weight phenolic resins. This new approach was found to reduce press cycles to 3-4 minutes for 7/16 inch (11.1 mm) waferboards and produce

a light-coloured panel. It is also possible that, using this process, methylolation of the kraft lignins would not be necessary, therefore saving a processing stage in the lignin adhesive preparation.

Several adhesive formulations have been proposed where instead of mixing or reacting the lignin with a pre-cook phenolic resin, the lignin is cooked directly with formaldehyde and phenol according to various cooking schemes and various orders of addition of chemical ingredients. (abstracts 38, 39, 41, 42, 43, 44, 50, 64, 65, 68, 72, 73). None of these appear to have progressed beyond the laboratory stage. In fact it may be easier to take advantage of the latest phenolic resin technology when using a phenolic resin copolymer. Janiga has recently claimed better results when SSL is mixed with phenol and formaldehyde before any substantial reaction between phenol and formaldehyde has taken place (abstract 72). Very little information on the energy required to cure this resin is provided.

Replacement of up to 90 percent of the phenol in the preparation of phenol-formaldehyde type of resins have been reported by Gupta et al (abstract 46). The lignin reactivity was increased by demethylolation with dichromate in presence of acetic acid prior to condensation with phenol and formaldehyde. Kambanis and Berchem have recently (abstract 73) proposed a less expensive process where phenol, formaldehyde and lignin are reacted in presence of potassium ferricyanide an oxidizing agent. It is claimed that in presence of this catalyst, no methylolation or purification of the kraft liquor is necessary. The use of oxygen or air as oxidizing agent for SSL prior to cooking with phenol and formaldehyde has also been proposed (abstract 60).

Lignin may also be used as a filler or extender for urea-formaldehyde resin. Most of the work on UF resin replacement refers to the use of SSL (abstracts 40, 42, 52, 53 and 70) which is generally less expensive than kraft lignin. UF resin is less expensive than PF and thus requires an inexpensive extender. Very little is known about the basic chemistry involved in lignin - UF resin condensation. Of course UF similar to PF resin contains methylo groups ($-CH_2OH$) which may condense with the aromatic groups of lignin if sufficient energy is provided. In Canada small amounts of SSL are already being tested commercially as UF resin extenders.

Recently lignin, either as lignosulfonate, kraft lignin or as a derivative such as hydroxypropylated lignin has been mixed with isocyanates to produce wood bonding resins (36, 54, 56, 63, 69). While some acceptable lignin-isocyanate formulations have been achieved in laboratory experiments, the amount of research devoted to these systems is limited. None of these binders appear to have found commercial applications yet. Isocyanates being highly reactive and having some tolerance to moisture present in wood, should be a beneficial additive to lignin formulations. However, high costs and some concerns about the handling of these potentially toxic chemicals remain a partial impediment to their rapid acceptance for glued wood products. Future work will be needed to determine how to improve

lignin reactivity to enhance co-polymezation capabilities with isocyanate. It is likely the instability of isocyanantes in aqueous resion systems will require either a two component formulation or the use of blocked isocyanate derivatives.

3.3.2 Literature Review

31 - H.M. McFarlane, 1964. Resins from spent sulfite liquor (SSL). Can. Pat. 696,732, To: Abitibi Power and Paper Co. Ltd., Iroquois Falls, Ont., Canada.

In accordance with this invention, an aldehyde (preferably formaldehyde) is partially reacted with a substance selected from the group consisting of urea, thiourea, melamine, phenol, creol, cresylic acid, resorcinol, naphthol and chlorophenol under alkaline conditions to provide a first liquor. Spent sulfite liquor (preferably decationized) is partially reacted with an aldehyde under acidic conditions to provide a second liquor. The first and second liquor are then mixed and reacted to provide a binder. The final pH of the binder is 3-6 with urea, thiourea or melamine and about 10 with phenolic.

32 - Roffael, E.; Rauch, W.; Beyer, S. 1971. Production of particleboards using SSL as binder. II. A new and Fast Method for the Production of Particleboards. Holz Roh-Werkstoff 25(5): 149-55.

The method is based upon the fact that the addition of an acid-tolerant phenolformaldehyde resin of the type "Novolak" increases the binding properties of sulfite lignin and leads, without using any post-thermal aging-step (tempering), to a practically water-insoluble thermosetting resin. A pH-range between 4 and 5 was found to be optimal. Using a combination of contact and radiofrequency the pressing time can be shortened up to 5-7 minutes with pressing temperature of 220 to 250°C.

33 - Roffael, E.; Rauch, W. 1972. Production of particleboards using SSL as binder. Possibilities of shortening the post-thermal treatment for SSL-bonded particleboards of 9 mm thickness. Holzforschung 26, (6): 197-202.

An improved method was devised for the production of these boards using contact heating and a short post thermal treatment. The technique is based on the finding that the addition of the small amount of a phenolic resin of the resol type increases the reactivity of the SSL lignin toward condensation so that thermosetting occurs within a relatively short period. The strength and swelling properties are dependent on the pH of the SSL/phenolic resin mixture.

34 - Roffael, E.; Rauch, W. 1973. Production of particleboard using SSL as binder. IV. Use of Sulfite Liquor in Combination with Alkaline Phenolic Resins. Holzforschung 27, (6): 214-217

Ammonium and sodium lignin sulfonates can be used as a partial extender for conventional alkaline phenolic resins for the production of particleboards. In the case of three-layer particleboards about 35% of the phenolic resin in the upper layers can be replaced by sodium lignin sulfonates without any significant decrease of the physico-mechanical properties of the boards. The pH value of sulfite liquor appears to have an optimum in the range of 7-10.

35 - Roffael, E; Rauch, W. 1975. Process for manufacturing a binder for wood-base materials through mixing of SSL with alkaline phenolic resins. German Pat. 2,406,807 DOS.

A process for manufacturing a binder for wood particleboards or the like by mixing SSL with alkaline phenolic resins is characterized in that mixing of the two components is made possible by freeing the SSL of disturbing amounts of alkaline-earth metal and heavy metal ions and adjusting to a pH of 7-13, preferably 9-12.

36 - Tashiro, T.; Ogawa, T., 1975. Compositions of lignin and isocyanates. Jap. Pat. 75158,651. ABIPC 48 (6) 6391.

Aqueous dispersions of use in making films, fibers and adhesives and building materials are prepared involving polyvinyl alcohol (PVA) and the reactive products of lignosulfonates with isocyanates such as hexamethylene diisocyanate.

37 - Forss, K.G., Fuhrmann, A.G.M. 1975 An adhesive for the manufacture of plywood particleboards and fiberboards. Brit. Pat. No. 1404536.

According to the invention an aqueous adhesive for use in the manufacture of plywood, particleboards and fiberboard was prepared comprising of lignosulphonates in which a minimum of 55% by weight of the lignosulphonate have a molecular weight in excess of 5000. For example, at 50 percent replacement of phenol formaldehyde with Na lignosulfonate, particleboard surpassing the requirement of the German Standard DIN 68761 are obtained using a press cycle of 60 sec/thickness (mm) at a press temperature of 215°C (This resin was later called Karatex see abstract 49).

38 - Enkvist T.U.E., 1975. kraft or soda black liquor adhesive and procedure for making the same. U.S. Pat. 3,864,291. To: Runebergsgatan 30 A. Helsinki.

Kraft or soda black liquors may be used for the manufacture of adhesives for plywood or particleboard in combination with a

rather small amount of phenol and formaldehyde, under proper reaction conditions. One part by weight of phenol and 4 parts of kraft or soda black liquor organic matter may be used. In an example, kraft black liquor is reacted with formaldehyde while in a separate vessel phenol is reacted with formaldehyde. The black liquor adhesive and phenol adhesive are then mixed. Examples are also given where the kraft, phenol and formaldehyde are cook in the same vessel. The preferred pH of the final adhesive is 8-10 after dilution 1:10 with water.

39 - Coyle, R.P. Particleboard, hardboard and plywood produced in combination with a lignosulfonate-phenol-formaldehyde glue system. U.S. Pat. 3,931,072. 1976. To: Champion International Corp.

The process involves forming a lignosulfonate-formaldehyde prepolymer by heating a solution of lignosulfonic acid salt with an alkali-metal hydroxide and then adding formaldehyde, thereafter adding phenol, followed by additional formaldehyde and heating. Sufficient alkali metal hydroxide is used to secure a glue system having a pH range of about 10.3 to 10.7. Examples are given for particleboards bonded with a phenolic resin containing 25 percent sodium lignosulfonate. These had mechanical properties comparable to the control particleboards bonded with pure phenolic.

40 - Willegger, W. N; Thiel H. G. 1976 Modified urea-formaldehyde resin adhesive. U.S. Pat. 3,994,850. CA:86(12)73967f. To: Champion International Corp.

A formaldehyde - sodium lignosulfonate - urea copolymer was prepared having reduced odor and imparting increased adhesive strength to fiber or particleboard composites when compared with commercial formaldehyde-urea resin adhesives. For example, a basic aqueous solution including HCHO, urea and lignosulfonate having a pH of 7.1 - 8.5 is heated at 65-95°C; acidified at pH of 5.0-6.5 and further heated at 88-98°C for a period of time sufficient to form an adhesive resin. The final pH of the resin is adjusted to 7.1 - 7.4 and urea is added to provide a HCHO: urea molar ratio of 1.2 - 1.7:1.

41 - Wennerblom, B.A.; Karlsson, A.H. 1976. Process for preparation of lignin resin. U.S. Pat. 3,940,352. To: Casco AB, Stockholm.

This process describes a two-step procedure for the preparation of a condensation product of lignosulfonate-phenol and -formaldehyde. The first step is an acid condensation of phenol and sulfite waste liquor in the presence of small amounts of formaldehyde at 80°C and pH of 0.2 to 4.0. The second step is an alkaline condensation step wherein the cooled reaction products of the first acid condensation step are further condensed under alkaline conditions at a temperature of at least

60°C by adding more formaldehyde and enough alkali so that the pH exceeds 7.0. The water content during the second step is 40-60 percent by weight based on sulfite waste liquor and phenol. Particleboard of 20 mm thickness were pressed 9-15 min at 160°C with a lignosulfonate-phenol and -formaldehyde adhesive containing approximately 33% sulfite liquor by solid weight. The panel had acceptable dry mechanical strength and low thickness swelling.

42 - Edler, F. 1977. Method for manufacturing amino-phenolic resin-based binder with addition of spent sulfite liquor (SSL). Swedish Pat. 397,834. To Edler & Co., Fargindustri AB. (Translation from Institute of Paper Chemistry, Appleton, Wis., U.S.A.).

A method for producing amino or phenolic resin-based adhesive products of use in particleboard production. Amino (such as urea) or phenolic monomers are condensed with HCHO and with SSL. Polyols (e.g. ethylene glycol) are added to ensure that the hydrophilic state of the condensation product is retained. The binder can incorporate large amounts of SSL while still exhibiting good bending properties.

43 - Saito, K. 1977. Lignin Adhesives. Jap. Pat. Kokai, 7,793,444.

A formaldehyde-lignin-phenol copolymer is prepared for particleboard binders by heating at 100°C for 30 minutes a mixture of 250 g lignin, 185 g HCHO, 75 g phenol, 25 g NaOH, 130 mls ethanol at a pH 9-9.5.

44 - Allan, G.G. 1978. Process for the partial substitution of ammonium lignosulfonate for phenol in phenolic-aldehyde resin adhesives. U.S. Pat. 4,127,544. To: Weyerhauser Co. CA90(16)122680a.

Process comprises dissolving a dry residue of ammonium-base SSL in phenol to form a reaction solution; heating this solution under autogenous pressure at 150°-300°C until a reaction mass forms (2-3 hours) and condensing the latter with formaldehyde (HCHO) in the presence of an aqueous alkali-metal hydroxide. The stroke cure time of this resin at 100°C was 20 seconds.

45 - Clarke, M.R.; Dolenko, A.J. 1978. Methylolated kraft lignin polymer resin. U.S. pat. 4,113,675.

A highly cross-linkable methylolated kraft lignin is provided for use as a high-wet-strength adhesive in the manufacture of particleboard and plywood and the like. The preparation involved methylolation of the kraft lignin black liquor at a pH of about 12, followed by acidification to pH 5 providing precipitation of lignin. The precipitate is allowed to settle and the supernatant liquid is decanted. The precipitated lignin

is then mixed with an acid curing PF resin and its pH adjusted at 2-7. Examples are provided where waferboard (11.1 mm of thickness) with good dry and wet bending properties were obtained using a press cycle of 5 minutes at a press platen of 204°C. The panels where bonded with 3 percent resin containing approximately 80 percent by weight of methylolated kraft lignin.

46 - Gupta, R.C.; Singh, S.P.; Jolly, S. 1978. Pehnol-lignin-Formaldehyde for Plywood. Holzforschung und Holzwervertung 30 (6) 109-112.

Thiolignin precipitated from black liquor of CHIR (pinus roxburghii) was used for developing adhesives for plywood. Thiolignin demethylated with dichromate in presence of acetic acid could be used to replace up to 90% of the phenol in the preparation of phenol-formaldehyde type of resins and the performance of plywood has been found somewhat better than with pure phenol formaldehyde resin.

47 - Dolenko, A.J.; Shields, J.A. 1978. Large scale production of powder adhesives based on kraft lignin. Technical Report 506ER. Forintek Canada Corp. Ottawa, Ont.

The feasibility of manufacturing modified kraft lignin adhesives under plant conditions was assessed. Approximately two tons of powdered adhesives were produced in cooperation with three industrial plants and subsequently tested in laboratory-fabricated waferboards.

The first stage of the program, the production of methylolated kraft lignin (MKL) was accomplished successfully with the use of existing facilities at a kraft paper mill. Samples of the MKL were subsequently blended with a commercial phenol-formaldehyde resin and the adhesives obtained were assessed in the laboratory. Based on current raw material prices and production costs including profit margins, it was estimated that a satisfactory adhesive could be produced at half the cost of presently used phenol-formaldehyde resins.

48 - Lehmann, G.; et al. 1979. Process for manufacturing cold wood glues. German Pat. 2,745,809. To: Badische Amilin & Soda-Fabrik AG.

Cold wood glues are prepared by bringing a UF resin solution (HCHO to urea molar ratio of at least 1.2:1; viscosity at 20°C of 500 to 1500 MPa.s) to a pH of at least 7.5 and a temperature of at least 40°C and mixing with appropriate quantities of SSL.

49 - Forss, K.G.; Fuhrmann, A.G.M. 1979. Finnish plywood, particleboard, and fiber - board made with a lignin based adhesive. Forest Prod. J. 29(7): 39-43. ABIPC 50:A6411

A lignin-based adhesive (called Karatex) was developed at the Finnish Pulp & Paper Research Institute. High-molecular weight

lignin derivatives are isolated from SSL or from black liquors by ultrafiltration and copolymerized during the hot-pressing stage with PF resin. This yields a strong water-resistant glue line. The adhesive contains 40-70% lignin. Full-scale trial runs yielded exterior-grade plywood meeting standard requirements. Use of this adhesive on Douglas- fir plywood resulted in wood failures exceeding 85% after both vacuum and boiling tests. Weather-resistant particle boards have been manufactured, using high-frequency (hf) or combined hf/contact heating, with pressing times of 10-12 second/mm. Fiberboards Comparison of their properties showed that they equalled those of boards made with ordinary commercial PF resin.

50 - Mitsui-Toatsu Chemicals Inc. 1980. Modified phenolic resin adhesives for fibreboards. Japan Pat. Kokai 137,120/80.

Lignosulfonates having molecular weight of 30,000 or less and carboxyl groups over 20 mole percent (based on phenylpropane units) are polymerized with phenol and HCHO to give adhesives for the manufacture of fiberboards. The lignosulfonates are oxidized with nitrobenzene. Fibreboards were pressed 5 min. at 190°C and 30 kg/sq. cm.

51 - Sudan, K.K. 1980. Waferboard Adhesives. Proceeding of the 14th Washington State University Symposium, Pullman, Washington.

A review of the progress made (to 1980) in the various adhesive systems used up to then for waferboard production. It describes the development of the spray-dried powder phenolics and modified phenolic powders in waferboard production. Mentions the use of acidified SSL powder.

52 - Edler, F.J. 1980. Sulfite spent liquor-urea-formaldehyde resin adhesive product. U.S. Pat 4,194,997.

An adhesive for use in making wood particleboard comprises 50-90 parts UF resin and 10-50 parts SSL. The SSL component has a pH of 3-10 prior to mixing, has a molar ratio of formaldehyde: urea of 1.0-1.8:1, a pH of 6-8, and a methylol content corresponding to a Witte number of 1.0-1.8. The SSL can be Ca-, Mg-, Na-, or ammonium-base, but contains a sufficient amount of a water-soluble ammonium salt of a strong acid to provide 0.2-4.0% by weight of ammonium ion (expressed as ammonia) based on the SSL solids in the final adhesive product. The ammonium ion can be provided by the use of ammonium-base liquor, or by adding an appropriate salt such as ammonium chloride or ammonium sulfate.

53 - Cassinotti, M.; Pizzi, A. 1981. Urea-formaldehyde resin-based adhesive containing calcium and/or ammonium lignosulfonate for preparing agglomerated wood panels. CA:96(12)86744n. European Pat. Appl. EP41745A1.

Adhesives for particleboards having good mechanical properties and low residual formaldehyde comprise a formaldehyde-urea copolymer containing calcium or ammonium lignosulfonates (50 percent in water).

54 - Glasser, W.G.; Hsu, O.H.H.; Reed, D.L.; Forte, R.C.; Wu, L.C.F. 1981. Lignin-derived polyols, polyisocyanates and polyurethanes. ACS symposium series. 172:311-338.

The preparation of oxypropylated maleated polyols from lignosulfonates for use as lignin-based polyurethane adhesives for wood is described. It is estimated that the lignin-based polyols could be sold for about 40¢/lb.(88¢/kg)

55 - Hollis, Jr. et al 1981. Lignin-containing resin adhesive. U.S. Pat. 4,303,562 to American Can. Company.

Novel lignin-phenol-formaldehyde resins, suitable for use as wood bonding adhesives, are provided by a two-step method which comprises reacting formaldehyde and phenol in the presence of an alkaline catalyst, thereafter reacting acid precondensed resin with sodium hydroxide, formaldehyde and a lignin concentrate having at least 40% solids and comprising lignin dissolved in (a) phenol and water or (b) phenol; water and sodium hydroxide or ammonia. The lignin to phenol weight ratio being less than 70:30 and more than 40:60. Press cycle of 6 minutes at 285°F(140°C) are reported for 6/16 inch (9.5 mm) thick plywood panels bonded with the lignin - PF resin.

56 - Lambuth, A.L.; 1981. Aqueous polyisocyanate-lignin adhesive. U.S. Pat. 4,279,788. To: Boise Cascade Corp. CA: 95(14) 1173 78g.

An aqueous polyisocyanate-lignin adhesive for use particularly in the manufacture of wood composition board comprises in admixture with each other an organic polyisocyanate and the lignin product resulting from the chemical pulping of lignocellulose. An example is given for the production of fiberboard bonded with 2.35% isocyanate prepolymer and 1.15% calcium spent sulfite liquor 50% solid. The panel had a MOR of 2453 psi (16.9 MPa) as compared to 2075 psi (14.3 MPa) for the control. An example is also given for a cold setting adhesive of lignin - polyvinyl - isocyanate composition.

57 - Calvé, 1. 1982. Fast curing kraft lignin for waferboards binders. CFS contract 1981-82, CFS/DSS project 45 (supplementary Report 1).Forintek Canada Corp.

A fast curing kraft lignin-phenolic adhesive was formulated. It is a mildly acidic resin dispersion formulated from an alkaline phenolic resin and kraft lignin preferably pre-reacted with formaldehyde. Waferboard of exterior grade quality could be produced using a press cycle of 22 sec/mm at 210°C press platen with 2.5 percent resin containing 70 percent kraft lignin. This is an improved adhesive system as compared to the slower curing kraft-phenolic resin system previously developed at Forintek (abstract 45).

58 - Calve, L; Troughton, G.E. 1984. 1982 Canadian Waferboard Symposium Proceedings Special publication SP 508E. Forintek Canada Corp.

The work on renewable adhesive at Forintek Canada Corp. is reviewed. A new fast curing ammonium based spent sulfite liquor (SSL) system copolymerized with phenol-formaldehyde resin is introduced (see abstract 74 of U.S. patent 4,579,892). Waferboard of exterior grade quality were produced with 2.5 percent resin containing 70 percent ammonium based SSL using a press cycle of 5 minutes and a press platen temperature of 210°C. The boards were light in color and presented no sticking problems.

59 - Go, T.A. 1984. 1982 Canadian Waferboard Symposium Proceedings Special publication SP 508E. Forintek Canada Corp.

Temfibre (Temfibre Inc.) Temiscaming, Quebec has bought the right to commercialize the adhesive developed at Forintek Canada Corp. from spent sulfite liquor (abstract 20). A successful waferboard plant trial was conducted with liquid ammomium based spent sulfite liquor (Tembind) replacing 50 percent of a commercial waferboard adhesive. Waferboards panels of 6.2 mm were produced with 2.5 - 2.7 percent resin with a press cycle of 2 minutes 40 seconds at a press temperature of 410°F (210°C).

60 - Sanyo-Kokusaku Pulp Co. Ltd. 1983. Phenolic resin-lignin adhesives. Japan Pat. Kokai 57,128,764/82.

Adhesives for hot-pressed wood laminates are prepared from phenol, formaldehyde and 10-50 percent (based on phenol) of lignosulfonate prepared by oxidizing spent sulfite liquor with air or oxygen at 140-180°C until the pH drops to 3-6. A mixture of 70 parts phenol, 75 parts lignosulfonate (40% solids, pH 4.2) 129 parts 37 percent formaldehyde and 61 parts water was mixed dropwise with 61 parts 50 percent NaOH at 85°C until its viscosity (42 percent solids, 25°C) reached 200-400 cp. The mixture was treated with 10 parts (per 100 parts resin) of coconut powder and 3 parts cross-linking agent. At a spread of

15 g/1900 sq. cm., pressing at 135°C and 10 kg/sq. cm. for 4 minutes and 20 minutes at room temperature, a laminate with adhesive strength 8.5 kg/sq. cm. and adhesive failure 85 percent was obtained.

61 - Calvé, L.; Brunette, G. 1982. Ammonium-based SSL for medium density fibreboard improved by copolymerization. Forintek Canada, Report 60-43-306.

Crude NH_4-based SSL was used to prepare medium density fibreboard for both interior and exterior use. Press times and temperatures (8 minutes and 230°C respectively) were greater than with UF adhesives and the resulting boards possessed low MOR. Properties would be improved by improving board density.

The use of a PF copolymer was found to significantly increase the MOR strength of the board as well as reduce press requirements. The NH_4SSL could replace up to 70 percent of the PF without greatly reducing its strength.

The unmodified NH_4SSL was far cheaper than the UF or PF adhesives, while the NH_4SSL-PF adhesive was comparable in price and quality to the UF adhesive but with significant reduction in formaldehyde emission.

62 - Rosenberg, G.N. 1982. Methylolated kraft lignin adhesives. Can. Pat. 1136793. To: MacMillan Bloedel Ltd., Can. CA:98(74148z).

The addition of a water-soluble PF copolymer to hydroxymethylated kraft lignin, obtained by treatment of black kraft liquors with formaldehyde, gave adhesives for use in the manufacture of wafer, wood strand or particleboards. A mixture of 50 percent PF resin, 50 percent hydroxymethylated kraft lignin was used. Press time: 6 minutes, press temperature: 210°C at 2.8 MPa.

63 - Glasser, W.G.; Saraf, V.P.; Newmann, W.H. 1982. Hydroxylpropylated lignin-isocyanate combinations as bonding agents for wood and cellulosic fibers. J. Adhesion, 14: 233-255.

Isolated kraft lignin (Indulin ATR-Cl, Westvaco) and steam explosion lignins can easily be liquefied by an oxyalkylation reaction with propylene oxide. Liquid lignin derivatives can be resolidified by cross-linking with bi-functional isocyanates. It appears that lignin can replace up to about one half of the isocyanate content of an isocyanate adhesive without loss in strength properties. At below 30 percent replacement, lignin-containing isocyanate binders have strength properties greater than that of the isocyanate control binder. While lignin contributes beneficially to the performance of isocyanate-bonded cellulose fiber assemblages, isocyanate-bonded wood particleboards seemed to suffer from the presence of lignin

or hydroxypropylated lignin derivatives. Unmodified steam explosion lignin performs as well as hydroxypropylated lignin in conjunction with isocyanates in terms of strength properties, or even slightly better.

64. - Janiga, E.R. 1983. Lignosulfonate-phenol-formaldehyde resin binder. U.S. Pat. 4,423,173 to Masonite Corp.

The resin is prepared by heating a mixture of lignosulfonate (LS), phenol and HCHO, the LS being added to the phenol and HCHO under alkaline conditions before a substantial degree of reaction between the phenol and HCHO has occurred and heating the mixture to form the polymer. The resin can also be used together with fibers in forming molded articles.

65 - Moreira, E.A.; Lossada, A.A.; Valenti, R.A. 1983. Adhesives for wood products from lignocellulosic residues. ATIPCA Congr. Tec. Celulosa y Papel (Buenos Aires). 2:141-156.

Lignosulfonates of high purity were recovered by ultrafiltration from spent neutral sulfite pulping liquors. The lignosulfonate-rich fraction was used for producing thermosetting adhesives for laminates and briquettes by two methods: a) by the addition of lignosulfonates or lignosulfonate/formaldehyde to phenolic resins and, b) by a phenol-lignosulfonate/formaldehyde reaction. Laminates were manufactured and tested. Products of both methods of preparation possess adhesive properties.

66 - Ayla, C.; Nimz, H.H. 1984. Use of waste liquor lignin for production of wood composites. Holz al Roh-Werkst. 42(11); 415-19.

A review with 18 references on the use of waste pulping liquor lignin in the production of various wood composites including the production of particleboard from SSL mixed with PF or UF resins.

67 - Muller, PC.; Glasser, W.G. 1984. Engineering plastics from lignin. VIII. Phenolic resin prepolymer synthesis and analysis. J. Adhesion, 17:157-174.

A sequential derivatization of lignin with formaldehyde and phenol was investigated as a means of enhancing lignin's reactivity in PF resins. Kraft lignin and two novel bioconversion lignins, steam explosion lignin (SEL) and acid hydrolysis lignin were chemically modified by sequential reaction with formaldehyde and phenol. The results with regard to the chemical structure of the phenolic resin prepolymers showed that the ability to hydroxymethylate and phenolate is related to lignin structure. Kraft lignin from pine proved to be more amenable to chemical modification with formaldehyde and phenol than either SEL from aspen or acid hydrolysis lignin from pine.

68 - Muller, P.C.; Kelley, S.S.; Glasser, W.G. J. 1984 Engineering plastics from lignin, IX. Phenolic resin systhesis and charaterization. J. Adhesion, 17:185-206.

The performance of PF resins formulated with lignin derivatives previously synthesized as phenolic resin prepolymers was evaluated by thermal analysis of the curing process and by a hard maple shear block test. At 54 and 60 percent phenol replacement levels respectively, kraft and steam explosion lignin-based resoles exhibited cure behavior very similar to a standard PF resin. Shear strength of kraft-based PF resins compare favourably with strength values of the pure PF resin of the lignin tested, kraft lignin consistently demonstrated superior performance as a pre-polymer in phenolic adhesives.

69 - Gaul, J., M.; Nguyen, T. 1984. Organic polyisocyanate-liquid aromatic epoxide-lignin adhesive binder compositions. U.S. Pat. 4,486,557. To: Atlantic Richfield Co.

An adhesive binder composition is provided for the preparation of lignocellulosic composite molded articles such as flake or particleboard. The binder composition comprises a liquid aromatic epoxide having one alpha epoxide group and/or aromatic or aliphatic-based multifunctional epoxide having 2 or more epoxide groups and an organic di- or polyisocyanate (MDI or PMDI). The source of lignin may be any SSL, kraft black liquor or acid precipitated kraft lignin. Pressing temperatures range from 140°C to 220°, preferably 160°C to 190°, the pressure from about 0.69 to 4.1 MPa for a period of from 1 to 10, preferably 3 to 5 minutes.

70 - Calvé, L.R.; Brunette, G.G. 1984. Reducing Formaldehyde Emission from Particleboard with Urea-Salt or Sulfite Liquor. Adhesive Age 27(9): 39-43.

Replacement of 45% UF with NH_4SSL reduced the resin cost by 28% and formaldehyde emission by 50%. The board still meet the CAN-3-0188,1-M78 Grade R requirements for interior grade particleboards. SSL had no adverse effect on UF resin curing properties. Unfortunately, it produced particleboards with lower IB although these were well above standard requirements.

71 - Pantyukov, V.P. ; El'Bert, A.A. 1985. Adhesive capacity of lignosulfonates. Leningrad Lesotekh. Aka. (2):69-71. CA 103, 7925j.

Mixtures of phenolic resins with less than or equal to 25 percent lignosulfonate were pressed at 160°C for 10 minutes to give materials exhibiting high mechanical strength. Optimum pressing conditions for compositions containing 25 percent Al lignosulfonate were: 150°C, 0.8 min./mm board thickness.

72 - Janiga, E.R. 1985. Method of bonding using a lignosulfonate-phenol-formaldehyde resin binder. U.S. Pat. 4,559,097. To: Masonite Corporation.

A method of manufacturing a lignosulfonate-phenol-formaldehyde resin includes heating a mixture of phenol-formaldehyde lignosulfonate and alkali at a temperature of 60°C to 100°C and a pH of 8-13 the lignosulfonate comprises about 5 to about 80 percent of the total weight of phenol, formaldehyde and lignosulfonate and the lignosulfonate is mixed with said phenol and formaldehyde before substantial reaction between phenol and formaldehyde. Waferboard sample were bonded with 2.5% resin containing 30 percent by weight of lignosulfonate. The panel of 11.1 mm thickness pressed 7 min. at 204°C had a modulus of rupture (MOR) of 4105-5455 psi (28.3-37.6 MPa).

73 - Kambanis, S.M.; et al 1985. Lignin-modified phenolic adhesives for pressed wood products. U.S. Pat. 4,537,941. To: Reichhold Ltd., Can.

An improved modified phenol-formaldehyde resin and a process for its preparation which contains kraft lignin (black liquor) is described. A small amount of potassium ferricyanide is included with the phenol. No methylolation or purification of the kraft liquor is necessary. The adhesive is used in the form of a dry powder. 2.5 percent of the resin, 1.5 percent wax are mixed with wood wafers and the mat is pressed at 204°C and 3375 kPa for 4 to 5 minutes. The boards pressed for 4 minutes had the following characteristics: MOR 24.8 MPa, MOE 365 MPa. MOR after accelerated aging: 13.8 MPa, swelling in water (24 hour soak test): 18 percent.

74 - Calvé, L.R.; Brunette, G. 186. Ammonium-base spent sulfite liquor-phenol formaldehyde thermosetting resin and method of binding lignocellulosic material employing same. U.S. Pat. 4,579,892. To: Forintek Canada Corp.

The ammonium spent sulfite liquor-phenol-formaldehyde (NH_4SSL-PF) thermosetting binder of this invention is inexpensive, fast curing and unlike previous techniques, can be produced in a one step operation. It does not require modification or addition of alkali or buffer. It has been found to have adhesion superior to those of NaSSL-PF and CaSSL-PF resins. The PF resin may be added directly to the acid NH_4SSL. The prefered PH of the resin is between 3-8. The acidic dispersion can also be used in powder form. Upon acidification, the phenolic resin copolymer get discolored and very light panel are obtained even when the adhesive resin contain up to 80 percent lignosulfonate (see abstract 58). Waferboard (11.1 mm thick) of exterior grade quality were produced at 50 percent phenolic resin replacement using a press cycle of 3 minutes at a press platen temperature of 210°C.

3.4 SECTION C. BIOCONVERSION LIGNINS (STEAM-EXPLODED, ACID HYDROLYSIS AND ENZYME LIGNINS) AS ADHESIVES IN WOOD PRODUCTS

3.4.1 Comments on Section C

Although very little work has been conducted to date on the use of bioconversion lignins in adhesives for wood products, some key experiments have been carried out which permit some conclusions to be drawn. In 1982, Calvé and Shields at Forintek (abstract 75) reported that steam explosion lignin performed similarly to kraft lignin and could be used as an extender for PF resin in the manufacture of exterior grade waferboard and plywood. Comparisons were made between enzymatic, alkali extracted and alcohol- extracted lignins. Using the Clarke and Dolenko process previously developed at Forintek (abstract 45), at 70% lignin replacement, a press cycle of 7 minutes was sufficient to produce a waferboard panel which exceeded the CSA minimum specifications for strength properties. Internal bond was however low as compared to results obtained previously with kraft lignin from softwood pulping (abstracts 57 and 76). This was an indication that the aspen steam explosion lignin evaluated was slightly less reactive than methylated kraft lignin. This was further verified by Glasser who reported (abstract 78) that the aspen lignin from the steam explosion process is less amenable to chemical modification with formaldehyde and phenol than kraft lignin from pine wood. This finding is not surprising since aspen lignin contains larger amounts of the less reactive syringyl (3,5 - dimethoxyphenyl) groups than kraft lignin. Partial demethylation of the syringyl unit is also believed to occur during kraft pulping.

On the positive side, since the former evaluation of the steam explosion lignin by Calvé and Shields in 1982 (abstract 75), significant progress in the area of lignin based adhesives has been achieved at the Eastern Laboratory of Forintek. Various techniques of reacting phenol and formaldehyde with lignin were evaluated, including a mixture of high and low molecular weight phenolics. A slightly acidic lignin-resin dispersion was found to cure 25 percent faster than previous resin systems (abstract 45). Preliminary results on steam explosion lignin have indicated that short press cycles of 4-5 minutes are possible using this new approach. This adhesive should be appropriate as a surface adhesive for waferboard/OSB (the waferboard industry produces a three-layer panel using a slower curing adhesive on the face-layers).

Further work at Forintek on steam explosion lignin (abstract 80) has indicated that the steam explosion process variables (temperature, time) as well as the presence or absence of catalysts (acid or oxidizing agent) have a definite effect on the reactivity of the lignin obtained. Adjusting these process parameters should facilitate the production of more reactive lignins, suitable for the manufacture of fast curing adhesives. If available in large quantities at a reasonable cost, a reactive lignin of controlled quality will have definite advantages over existing lignin stocks from pulp and paper mills.

3.4.2 Section C - Literature Review

75 - Calvé, L.; Shields, J.A. 1982. Bioconversion lignins as waferboard and plywood adhesives. Proc. 4th Bioenergy R&D Seminar; March, 1982. (Winnipeg, Canada) pp 403-407.

Lignin fractions from steam-exploded aspen chips were obtained by ethanol extraction, dilute alkali extraction and as a residue after enzymatic hydrolysis. When mixed with an acid-curing PF resole having a mole ratio of phenol to formaldehyde 1:1.8 in the proportion 70 percent lignin, 30 percent resole and pressing at 210°C for 7 minutes, all boards exceeded the CSA minimum specifications for strength characteristics. If shorter press times are required, a 60/40 lignin-PF resole ratio could be used. For waferboard, alkali-extracted lignin was superior to the other lignin fractions. For plywood, enzyme lignin performed best. All lignins performed best when methylolated.

76 - Glasser, W.G.; Saraf, V.P.; Newman, W.H. 1982. Hydroxypropylated lignin-isocyanate combinations as bonding agents for wood and cellulose fibers. J. Adhesion, 14: 233-255.

Isolated kraft lignin and steam explosion lignins can easily be liquified by an oxyalkylation reaction with propylene oxide. Liquid lignin derivatives can be resolidified by cross-linking with bi-functional isocyanates. While lignin contributes beneficially to the performance of isocyanate - bonded cellulose fiber assemblages, isocyanate-bonded wood particle boards seem to suffer from the presence of lignin or hydroxy propylated lignin derivatives. The strength and swelling properties of particle board suffered in relation to lignin content.

77 - Muller, P.C.; Kelley, S.S.; Glasser, W.G. 1984. Engineering plastics from lignin IX. Phenolic resin synthesis and characterization. J. Adhesion, 17:185-206.

The performance of PF resins, formulated with lignin derivatives previously synthesized as phenolic resin prepolymers was evaluated by thermal analysis of the curing process and by a hard maple shear block test. At 54 and 60 percent phenol replacement levels respectively, kraft and steam explosion lignin (SEL)-based resoles exhibited cure behaviour very similar to a standard PF resin. Shear strength of kraft lignin and SEL-based PF resins compare favorably with strength values of the pure PF resin. The phenolic resin formulated with SEL exhibited strength values which were slightly slower than those of the pure and kraft lignin-based resins.

This study shows that unfractionated lignin can indeed by incorporated into PF resins with equal performance as their unextended counterparts. However, this incorporation into the network structure may require (expensive) prepolymer synthesis by derivatization with formaldehyde and phenol.

78 - Muller, P.C.; Glasser, W.G. Engineering plastics from lignin. VIII. Pehnolic resin prepolymer synthesis and analysis. J. Adhesion 17:157-174.

A sequential reaction of lignin with formaldehyde and phenol was investigated as a means of enhancing lignin's reactivity in PF resins. Kraft lignin (KL) and two novel bioconversion lignins, i.e. steam explosion (SEL) and acid (sulfuric acid) hydrolysis lignin (AHL) were chemically modified by sequential reaction with formaldehyde and phenol. The results showed that the ability to hydroxymethylate and phenolate is related to lignin structure. Kraft lignin from pine wood proved to be more amenable to chemical modification (more reactive) with formaldehyde and phenol than was either SEL from aspen or AHL from pine.

79 - Gardner, J.G.; Sellers, Jr. T. 1986. Formulation of a lignin-based plywood adhesive from steam-exploded mixed hardwood lignin. Forest products J. 36(5) 61-66.

Steam-exploded mixed hardwood lignin was chosen to formulate an adhesive to glue southern pine plywood. Three lignin replacement procedures were examined to assess lignin's effect on bond quality. Adhesive application parameters approximated those used in the commercial manufacture of southern pine plywood. Plywood shear strengths with steam-exploded lignin-based adhesives were at least as good as those with the phenolic control. Wood failure however was lower.

80 - Forintek Canada Corp. 1983. Effect of Steam explosion process parameters on lignin reactivity. Eastern Forintek Lab. Unpublished Results.

Steam exploded lignins were prepared under various steam explosion processing conditions with or without the presence of a catalyst. The adhesive properties of the various lignins were partially evaluated for the production of waferboard. The test results have indicated that the steam explosion process variable as well as the presence or absence of catalyst have a definite effect on the reactivity of the lignin obtained. There are some indications that the reactivity of the lignin could be improved by adjusting these process parameters.

3.5 PRIMARY RESEARCHERS AND ORGANIZATIONS CURRENTLY ACTIVE IN LIGNIN ADHESIVES

Our literature review has identified a large number of individuals who over the last two decades have worked on lignin adhesive developments. From this group only a limited number are presently active in this field of study. Presumably part of the reason for decreased research activity related both to lower cost and increased availability of petroleum supplies which in turn results in lower and more stable phenolic resin prices.

The following lists primary researchers and organizations which to our knowledge are still active to some extent in lignin adhesive research.

Researcher	Organization	Country	Activity
L. Calve'	Forintek Canada Corp.	Canada	- SSL-PF adhesives - bioconversion adhesives
M.R. Clarke	Forintek Canada Corp.	Canada	- Kraft lignin adhesives
K.C. Shen	Consultant	Canada	- SSL adhesives
K.C. Shen	Pulp and Paper Research Institute of Canada	Canada	- lignin structure and application
A. Campbell	University of Idaho	U.S.A.	- lignin fractionation and adhesive development
H. Chum	Solar Energy Research Institute	U.S.A.	- bioconversion lignin for energy and polymeric products
R. Gillespie	U.S. Forest Products Laboratory (Madison, WI)	U.S.A.	- lignin adhesives
W. Glasser	Virginia Polytech Institute and State University	U.S.A.	- lignin adhesives and polymers
S. Lin	Reed Lignin Inc.	U.S.A.	- SSL and kraft lignin modifications
R. Young	University of Wisconsin	U.S.A.	- pulping lignins and adhesive development
I. Abe	University of Mie	Japan	- phenolic modification of lignin for adhesives

K. Forss	Finnish Pulp and Paper Research Institute	Finland	- Kraft and SSL lignin polymers
H. Nimz	Polymer Institute, University of Karlsruke	W. Germany	- SSL lignin adhesives
E. Roffael	Wilhelm Klauditz Institute	W. Germany	- Kraft and SSL lignin adhesives

4.0 PART II

WOOD ADHESIVE APPLICATION AND PROPERTY REQUIREMENTS

4.1 ADHESIVE PROCESS REQUIREMENTS FOR SPECIFIC WOOD PRODUCTS

It is well recognized that both chemical reactivity and ultimate cure properties of an adhesive are critical factors in wood composite bonding. In contrast, the role of the manufacturing process in defining adhesive requirements often is underestimated. As various wood composite developments have taken place, a variety of adhesive application systems have evolved. Many of these systems have been designed to accomodate the shape, size and type of wood material to be bonded. A common feature of many present application techniques is that they involve batch operations where adhesive is applied to the wood units which then are processed through a layup and pressing schedule involving multi-opening presses. Future trends appear to favour use of more continuous pressing equipment which may require changes in adhesive application techniques.

Adhesive requirements tend to be specific for the particular application process. The following describes, in general terms, the bonding process stages and adhesive requirements for manufacturing a number of wood composite products.

4.1.1 Plywood/Laminated Veneer Lumber (LVL)

In North America, plywood is almost exclusively bonded with PF adhesive, resulting in a product which is marketed as a fully exterior grade panel. The adhesive is applied in a liquid form to a dried (< five percent m.c.) veneer surface. To overcome the tendency of resin to overpenetrate porous wood surfaces, and to meet the requirements of the plywood manufacturing process, the adhesive is applied not as a neat resin but rather is combined with extenders and fillers to form a glue mix. A typical plywood glue mix is given in Table 5. The resin portion of this glue mix usually consists of a high molecular weight PF polymer of formaldehyde to phenol ratio in the range 1.9 to 2.1. To insure solubility in aqueous solutions these resins contain substantial amounts of NaOH (approximately 25 percent by weight of resin solids). The choice of additives and the glue mixing procedures depend upon material cost factors, mix viscosity desired and the transfer and assembly time properties required during bonding. Depending on mill operations, wood species, mill temperature and humidity conditions, minor variations may take place in this formulation.

Table 5

Typical Canadian Plywood Glue Mix

PF plywood resin*	2,519 lbs
water	1,055 lbs
modal filler	350 lbs
MBX-10 filler	200 lbs
mix - 5 minutes	
wheat flour	264 lbs
soda ash	176 lbs
mix - 20 minutes	
PF plywood resin*	1,807 lbs
water	490 lbs
TOTAL	6,861 lbs

TOTAL SOLIDS	42.2%
TOTAL PF SOLIDS	22.8%

* Containing 35% PF solids, 9% NaOH and 56% water

Glue mixes are usually applied by either a roller, spray or curtain coater apparatus with almost the total surface being covered with a continuous film of glue. The roller system is commonly used to apply glue to both sides of a veneer at the same time, while the other two systems, which are more adapted to automated assembly lines, apply the adhesive on one side of a veneer. Curtain coaters have decreased in popularity over the last few years because of difficulties in maintaining a thin, continuous film of glue during start and stop line operations. Recently, a new foamed glue application system has been introduced into several American and one Canadian plywood mill (North Central Plywood, Prince George, B.C.). While foamed glues offer potential savings by allowing reduced waste and spread level reductions, further mill experience is needed to determine if this system will become commonplace in plywood operations.

For proper roller applications, plywood mixes need a viscosity in the range of 1500 to 3000 centipose (cps). The glue mix must also be designed to provide tack and prevent overpenetration during prepressing while limiting dryout at longer assembly times. Good transfer of glue from one side of the veneer to the adjacent veneer is essential during panel pressing. Moisture in the glue mix and the viscosity controlling behaviour of the wheat flour extender are critical to effectively achieve these requirements.

Glue mix requirements for spray systems are different from roller systems in that lower glue mix viscosity is needed and proper spray droplet formation is essential to obtain adequate adhesive coverage of the veneer. Consequently, wheat flour content is often much lower in spray mixes while small amounts of surfactants may be needed to enhance the spray pattern.

Cure of PF plywood adhesives requires hot pressing, usually at a temperature of 140 to 160°C and pressures of 1.04 to 1.38 MPa. Pressing pressures depend upon wood density and veneer quality with higher density species and rougher veneer requiring higher pressures. These temperatures and pressures are the prime reason that veneers must be dried to low m.c. and that glue solids must be above 40 percent. During bonding, the PF adhesive, which contains a large number of reactive functional groups, both bonds with reactive sites on the wood surface and reacts with other PF molecules to give a highly cross-linked, strong, wood-adhesive bond. Another requirement for good quality bonds is that adhesive must penetrate partially into the cell wall layer on the wood surface. When destructively tested under wet conditions this bond will exhibit high shear strength and high wood failure. Table 6 lists some of the bonding variables in plywood manufacture.

Since LVL is also produced using veneer but with parallel orientation of plies, many of the adhesive requirements are similar to those of

Table 6

Variables in Plywood Bonding

Variable	Common Range
Resin solids	21 - 30%
Spread level	21.5 - 30.0 kg/1000 m^2 double glueline
Prepress time	2 - 5 min.
Press temperature	140 - 170°C
Press pressure	1.04 - 1.38 MPa
Press time (12.5 mm/2 panels per opening)	7 - 8 min.

plywood. One feature of difference is that LVL most often is manufactured as a thick panel and consequently greater care must be taken to limit moisture in the panel and to accelerate cure speed if possible. Glue mixes for LVL thus frequently contain resorcinol or tannin additives to reduce cure time while also containing more resin solids.

4.1.2 Waferboard/OSB

Commercial waferboard and OSB are manufactured almost exclusively with PF adhesives. For limited periods mills have also tried to incorporate either kraft or sulfite lignins into these PF adhesives and in more recent times have made some boards with isocyanate adhesives either in the core or throughout the whole panel.

Both the high pressing temperatures (210°C) and pressures 3.45 MPa utilized in the manufacture of PF bonded waferboard/OSB require wood furnish dried to a low m.c. (often < three percent). The primary differences between OSB and waferboard products are the longer/thinner flakes and the orientation factor of OSB panels. While this provides superior structural properties to OSB, the differences in terms of adhesive bonding requirements are minimal. The main differences in adhesive application requirements occur in these products when the choice is between powder and liquid adhesives.

Powdered PF adhesives are favoured in waferboard for two reasons: they add no water to the mat and provide good adhesive distribution with the slow blender speeds needed to prevent flake damage. Powders have the disadvantages of being dusty and more expensive than liquids. Since resin distribution directly influences waferboard/OSB properties, most mills have chosen the powder system for board manufacture.

Powdered resins need to be formulated to have proper tack and particle size distribution to adhere to dry flakes. Typical powdered PF adhesive properties are given in Table 7. With present, resin application levels of about two percent based on dry wood weight, many of these resin particles readily adhere to these flakes due to mechanical or electrostatic forces. The addition of slack wax or wax emulsion during resin blending also helps to retain resin powder on the flakes. This powder must be sufficiently tacky to remain attached to the flakes during orientation and mat formation. The use of thin flakes results in a large surface area to be bonded, with only a portion of this area being covered with resin. Thus, in contrast to veneer bonding where continuous adhesive films are formed, waferboard/OSB is bonded in a spot-like fashion, making resin distribution a critical factor determining board quality. Particle size distribution of the powder is one parameter influencing resin efficiency. If powder particles are large, total adhesive surface area is small and flake coverage becomes more limited. If resin particles become too small, many may fall within the cracks and rough areas of the flakes and be unable to make good contact with adjoining flakes during board pressing.

Table 7

Typical Powdered PF Properties

Apparent density (g/cc)		0.32 - 0.38
Stroke cure (seconds at 120°C)		30 - 50
pH (5 g in 100 ml H_2O)		8.5 - 9.7
Particle size distribution - % retained on:		
	200 mesh screen	9 - 12%
	325 mesh screen	30 - 33%
	fines	52 - 65%

Both adhesive flow and cure speed are important properties governing the performance of powdered flakeboard adhesives. The cure rate must be optimized so that cure is sufficiently rapid to achieve fast press times but not so rapid that the surface layer cures before the mat has been compressed to its target thickness. This would result in precure, giving the panel a weak surface layer. One method of reducing precure possibilities with faster curing resins is to increase press closing rates. However, this affects density distribution in the panel, causing a more dense surface layer which if carried to extremes can adversely affect board properties. Precure is more commonly overcome by using separate face and core resins, with the former being slower curing than the latter.

Powdered adhesive must flow adequately to achieve transfer and penetration into the flakes necessary to produce strong, durable bonds. To achieve this, PF powder must be formulated to partially melt and flow at the temperature and pressure conditions encountered during waferboard/OSB manufacture. Experience has shown that reduced powder flow inhibits proper bond formation. The optimum degree of flow properties needed for successful board preparation, however, has not been quantified.

Both cure and flow in powdered adhesives are governed by adhesive formulation and method of resin preparation. Cure speed often is inversely related to flow capabilities. Factors such as formaldehyde to phenol molar ratio, average molecular weight and molecular weight distribution, particle size, functional groups present and salt content all contribute to cure and flow behaviour.

While liquid adhesives have been tried in waferboard production, difficulties have been encountered in achieving adequate resin distribution. This problem is associated more with design of a system for efficiently spraying and blending large flakes. As OSB production increases, more opportunity exists for liquid resin applications because of the presence of longer and thinner flakes which allow the use of higher rotation speeds on blenders. Liquid PF adhesives for spraying onto flakes must be formulated to be of low viscosity at high solids content. These liquids must wet the flake surface but not overpenetrate it. Adhesives having a rapid increase in viscosity upon contacting the flake should be beneficial for preventing overpenetration. This could result if water present in the adhesive is either vapourized during spraying or rapidly migrates into the wood as the spray droplet wets the flake surface. Adhesive flow is then influenced by the application of heat and pressure during board manufacture.

4.1.3 Particleboard

Particleboard markets in North America are such that UF adhesives are the commonly used binder. Resin contents of at least five percent are necessary to insure service integrity of the board product. Often, three-layer boards are produced consisting of a hard surface layer of fine particles containing up to 10 percent adhesive. Since board

furnish is primarily residue material, a mixture of species often is present. Urea formaldehyde adhesives, being acid catalyzed, have a cure rate sensitivity to wood acidity. Cure pH should ideally be about 3.5. Thus, care is needed to insure that the resin used contains sufficient catalyst or buffer to develop proper cure or prevent precure behaviour in the resin.

These adhesives are applied as 50 to 65 percent solids resins through a spray nozzle onto dry particles. Spraying is accomplished by either air-assisted, airless or spinning disk methods. Resin viscosities in the range of 100 to 300 cps are necessary to achieve appropriate atomization and droplet size for particle coverage. The large surface area presented by the particles results in droplets covering only part of the total wood surface. Agitation of these particles in the blender during spraying allows distribution of the adhesive by either exposing new particles to the spray or by transferring resin from particle to particle by mechanical contact. While the adhesive needs to wet the particle, overpenetration must be prevented to insure efficient adhesive use. Resin efficiency is in part dependent on blender design with long retention time blenders being better resin distributors than short retention time ones. During mat formation and prepressing, resin tack is a necessary property for insuring the mat remains together during transfer into the press. To achieve proper tack and flow within a resin often requires some compromise with cure speed or the addition of special additives.

The formaldehyde emission issue has been of particular concern to particleboard because of the prevalent use of this material in interior living spaces (i.e., walls, floors, furniture). Consequently, UF adhesive developments have recently focussed on lowering F/U molar ratios or incorporation of melamine, isocyanate, lignin or phenolic compounds into resin formulations in order to reduce formaldehyde emissions.

4.1.4 Medium Density Fiberboard (MDF)

Medium density fiberboard is a rapidly expanding wood composite sector. At present, almost all MDF boards are manufactured with UF adhesives. One of the most critical steps in MDF manufacture is the application of resin to fiber. Resin contents of 6 to 10 percent have to be metered onto fiber having a surface area much greater than that of particleboard, in a uniform and controlled manner. Early production plants used a blender system similar to particleboard where resin is sprayed onto refined, dry fiber. Resins having F/U molar ratio, concentrations, buffering capacity and viscosity similar to particleboard resins are utilized. The presence of resin spots on finished board surfaces is a common occurrence with this blending method and is related to the inability to transfer resin adequately to all fiber surfaces.

More recently, blowline blending techniques have been favoured for MDF resin applications. In this technique, resin is added to fiber in the blowline section (usually by high pressure steam spraying) between the

refiner and the flash tube drier. This fiber is still wet and hot when resin is applied, resulting in more tacky fibers but better resin distribution. Because of the conditions in the blowline, there is a greater opportunity for diffusion of resin into the fibers and precure of the UF adhesive during the short duration, high temperature drying. Buffering agents are usually included to limit precure and maintain flow properties. Blowline methods are favoured because of ease of maintenance and elimination of resin spotting. Additionally, blowline blending techniques can accomodate higher resin viscosities (i.e., up to 500 cps) compared to the 100 cps limit for standard spray blending.

4.1.5 Laminated Lumber Products

For structural, exterior applications, to which the present discussion will be limited, large laminated lumber products are almost exclusively bonded with phenol-resorcinol-formaldehyde (PRF) adhesives. These are two component adhesives, mixed just prior to use and cured under ambient or elevated temperatures. One component consists of PRF polymer in aqueous solution, while the other component comprises a powder catalyst containing a mixture of filler and paraformaldehyde. Sometimes this second component is dispensed in an aqueous solution. The resulting PRF mixture is applied either by roller or extruder with solution viscosities in the range of 500 to 2,000 cps being desirable. The adhesive formulation must have appropriate dryout resistance and flow properties to allow time for application to a number of lumber pieces and then assembly and pressure application to form a laminated product. When extruders are used to apply adhesive it is essential to maintain sufficient resin flow so that the extruded ribbons spread out to completely cover the wood surface during bonding. Formation of a continuous glueline in these laminations helps to ensure bond quality, durability and bond reliability for these high valued, structural products.

A newer type wood composite lumber product is Parallam. This product is produced from long veneer strips, oriented in a parallel fashion to simulate the grain direction of wood. Since much of this board production process is proprietary, it is difficult to discuss the adhesive requirements for this product in a fully knowledgeable manner. Based on limited information, we believe the process utilizes waste veneer which is chopped into one-mm-wide strips ranging from two to eight feet in length. These strips are covered with PF adhesives by submerging the wood strips into a resin bath. The adhesive must be of sufficiently low viscosity to readily coat these strips. In the final product, most strips are completely covered with adhesives, which means that substantial resin contents must be used in the board (estimate about 6 to 10 percent adhesive). The board is assembled as a continuous billet pressed under high pressures and cured using microwave energy. With this system, total m.c. in the board must be kept below about 14 percent to prevent arcing during the curing process.

4.1.6 Comparative Adhesive Usages

The differences in adhesive application and bonding requirements for different products in part relates to the surface area to be bonded. Table 8 compares adhesive usage for lumber laminates, veneer, flakes and fibers. Note that surface area to be covered differs by a factor of about 2,400 when going from lumber to fiber bonding, while the resin weight coverage varies by only about 3.5-fold for the same volume of wood. This large difference between area to be bonded and adhesive amounts further emphasizes the importance of good resin distribution techniques in bonding flake or fiberous composites.

A summary of adhesive requirements for wood products discussed above are presented in Table 9. Many of the differences evident are directly related to the application needs for a particular product.

Table 8

Comparison of Adhesive Usage in Consolidating One Cubic Foot of Various Wood Elements of Douglas-fir, Original Density 28 lbs/cubic foot (Marra, 1980)

Wood Element	Bond Area (sq.ft.)	Lbs. Resin (MSGL)	Lbs. Resin (cu.ft. wood)	Lbs. Resin (lb. wood)
1-in. thick boards[1]	11	39	0.43	0.015
0.1-in. thick veneer[2]	119	7.5	0.89	0.032
0.0050-in. thick wafers[3,4]	240	5.8	1.40	.050
0.010-in. thick flakes[3,4]	1,200	1.2	1.40	.050
0.001-in. thick fibers[3,4]	24,000	0.05	1.40	.050

1 Lumber spread @ 60 lb/MSGL, adhesive @ 65% resin solids.

2 Veneer spread @ 30 lb/MSGL, adhesvie @ 25% resin solids.

3 Wafers, flakes and fibers blended with 5% resin solids.

4 Assuming no compaction.

Table 9

Range of Application Parameters for Adhesives in Specific Wood Products

Parameter	Product					
	Plywood (PF)	Waferboard/OSB (PF)		Particleboard (UF)	MDF (UF)	Structural Laminates (PF)
		liquid	powder			
Solids Content (%)	40-50	45-55	100	50-65	50-65	40-50
Viscosity (cps)	1,000-3,000	25-100	-	50-150	50-500	500-2000
Average weight molecular weight (M_W)	2500	1200	1000	300	300	800
Molecular weight range	300-20,000	94-15,000	94-15,000	200-600	200-600	150-12,000
Press pressure (MPa)	1.05-1.40	3.45	3.45	2.10-3.45	3.45-4.15	0.7-1.4
Press temp. (°C)	140-170	210	210	140-170	140-170	40-150

4.2 POLYMER AND ADHESIVE PROPERTIES INFLUENCING BOND PERFORMANCE

4.2.1 Polymer Properties

Adhesive properties are governed to a large extent by the chemical and physical structure of the polymer system present. High volume wood adhesives such as PF or UF are thermosetting polymers which incorporate formaldehyde as one active component. These water soluble adhesives have several application characteristics which make them suitable for large scale manufacturing processes while also providing the required product performance properties. Many of these important polymer features can be categorized into four main areas. These are discussed in the following sections, together with a comparison of corresponding features in lignins.

4.2.1.1 Reactive Functionality

Reactive functional groups provide the sites for molecules to link and form higher molecular weight species, ultimately leading to a strong, dense polymer structure. The degree of polymer chain branching and cross-linking provides strength and rigidity to these adhesives. For true cross-linking to occur, the molecular species must have a reactive functionality greater than 2.0.

Based on its chemical structure, phenol provides three highly reactive sites through which it can react with formaldehyde to form methylolated addition products. These methylolated structures can then condense further to form polymers. Theoretically, a molar ratio of F:P of 1.5:1.0 is the optimum combination to give a completely cross-linked system. In reality, it is impossible to achieve a completely cross-linked structure and, while prepolymers with up to 3:1 ratio of F:P are possible, ratios of 1.5 to 2.5:1.0 have proven most useful as wood adhesives. Since reactive positions in phenol are spaced symmetrically around the molecule, good opportunities exist for both linear and branch polymer chain extension.

Under alkaline conditions, methylolation of phenol occurs rapidly at temperatures of about 60°C, while condensation reactions, leading to cross-linked polymer structures, require temperatures above 100°C preferably about 130°C to achieve relatively fast cure. With acidic catalysis, condensation reactions giving cross-linked structures occur rapidly, even at room temperature. Unfortunately, most PF adhesives are insoluble in acid solutions and the high acidity is severely damaging to wood.

Urea has four potentially active sites capable of reaction with formaldehyde, thus affording possibilities for a highly cross-linked system. Common practice has shown the most suitable wood adhesives have molar F:U of 1.2 to 2.2:1.0. This combination allows a compromise between achieving high strength and maintaining low formaldehyde emissions. Urea formaldehyde resin formation is a two-stage process involving first the addition of formaldehyde to urea to form methylol ureas, followed by the condensation polymerization reactions, which form the higher molecular weight compounds.

Methylolation is accomplished under mildly alkaline conditions, with the mixture being adjusted to moderately acid condition for condensation and cure. Cure can be achieved at room temperature, but usually press temperatures of about 120 to 150°C are used to insure fast pressing. The primary disadvantage of UF systems is their sensitivity to both heat and moisture, both causing bond deterioration and formaldehyde emissions.

It should be recognized that both PF and UF adhesives are synthetic adhesives which have been polymerized in a controlled fashion from monomers in a manner that attempts to maximize reactivity. In contrast, lignins already are mixtures of partially or highly polymerized structures, where the number of active sites available for reaction is limited. Depending on the wood species and the lignin recovery process, the chemical reactivity of lignin varies. Some type of co-reaction either with formaldehyde or other cross-linking agents usually is needed to develop useful lignin adhesives (Figure 3). Most often cure temperatures above 160°C are required to achieve adequate cross-linking.

Reactivity of lignins is controlled largely by their structure and the degree of polymerization. As a representative of phenylpropane natural polymers, lignin exhibits a strong phenolic character in both addition and condensation reactions. Although lignin structures are complex, elemental and functional group analysis provides some comparison of relative differences between various isolated lignins. Table 10 is a compilation of data from several sources where lignin yield is a function of the isolation method. Of note is the variation in OCH_3 content which results from differences between softwood and hardwood lignins, the latter containing some syringy/aromatic units that have an extra OCH_3 substituted position (Figure 4). The higher carbon content, number of phenolic hydroxyls and lower total hydroxyls of acid hydrolysis and organosolv aspen lignin suggest that some hydrolysis of alkyl-aryl ether linkages followed by secondary condensation has occurred during processing and isolation. Steam exploded lignin, on the basis of increased phenolic hydroxyls, also shows signs of undergoing some hydrolysis during recovery.

The value of lignin products as adhesives also is indicated by formaldehyde consumption values, which show site reactivity in this polymer. In general, kraft lignin and organosolv lignin have a similar uptake of formaldehyde per unit weight of material, a value which is about 1/3 of the formaldehyde uptake of phenol. A second indication of lignin reactivity is the rate of formation of higher molecular weight polymers, since this differentiates between structures having sites forming only formaldehyde addition products and those polymers with sites which can condense to form chain extended or cross-linked polymers.

4.2.1.2 Molecular Weight and Molecular Weight Distribution

Molecular weight characteristics influence adhesive properties such as viscosity and cure time. Condensation polymerization often results in a distribution of units with varying molecular weights. These can be

Table 10

Chemical Characteristics for a Number of Lignin Materials*

Lignin Type	Elemental and Functional Group Composition (percent)					
	C	H	OCH_3	Total OH	Phenolic OH	Lignin Content**
Milled wood lignin						
red alder	57.2	5.8	18.2	10.1	3.27	40-50
Acid (H_2SO_4) hydrolysis lignin						
aspen	64.4	5.8	22.8	8.8	5.4	80-90
Steam explosion lignin						
aspen	61.9	5.3	18.2	9.6	4.3	70-90
poplar	62.3	5.7	15.0	9.8	4.3	70-90
Organosolv lignin						
aspen	66.4	5.9	20.1	8.1	5.4	50
Kraft lignin						
pine	61.6	5.9	14.0	10.5	2.8	75

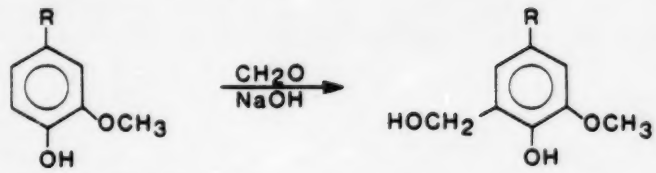
* Taken from Glasser, 1981; Glasser et al., 1983; Chum et al., 1985.

** Some carbohydrate present due to extractive process for recovery.

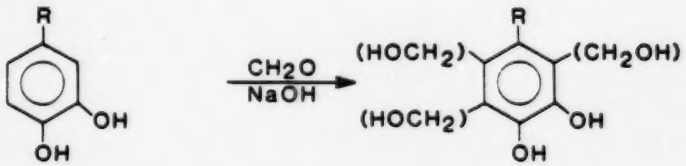
NOTE: Steam explosion and organosolv delignification processes are best qualified for producing homogeneous lignin fractions of suitably pure character.

Higher carbon content and lower hydroxyls for acid hydrolysis and organosolv lignin suggest secondary condensation during processing.

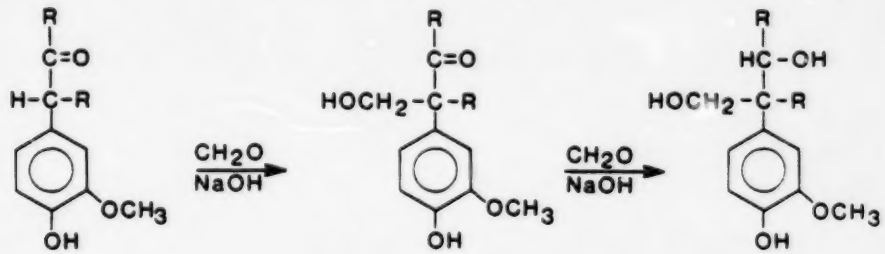
A. Methylolation of guaiacyl units.



B. Methylolation of Catechol units.



C. Methylolation of the side chain alpha to a carbonyl followed by reduction of the carbonyl.



D. Methylolation of the side chain at the beta position.

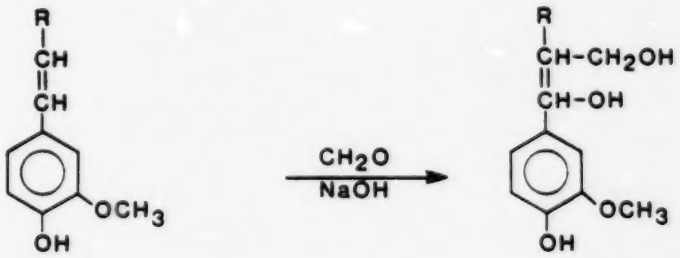
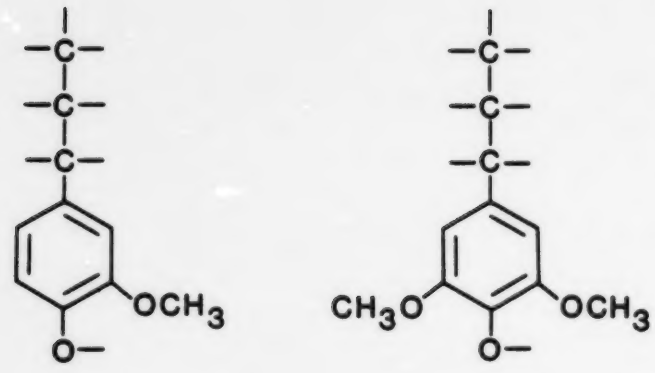


Figure 3. Representative reactions that can occur between lignin and formaldehyde in alkaline solutions (Sutcliffe, 1986).



Guaiacyl Unit

Syringyl Unit

Figure 4. Common aromatic unit structures present in lignin.

defined in terms of an average number ($\overline{M}_N$) or an average molecular weight ($\overline{M}_W$). A more useful means of representing molecular weight properties is through a distribution curve, which provides an overall picture of molecular size range. Table 11 lists molecular weight averages and molecular weight ranges for PF, UF, and several lignin polymers.

Phenol formaldehyde adhesives are synthesized to specific molecular weight ranges depending upon their intended application. Plywood and laminating PFs have the highest $\overline{M}_N$ and contain a wide distribution of molecular weight species (ranging from 300 to 20,000). Waferboard/OSB PFs have lower $\overline{M}_N$ ($\approx$1,400) with a greater proportion of lower molecular weight molecules in the mixture. Particleboard PF adhesives tend to be more homogeneous in molecular weight with $\overline{M}_N \approx 800$ and ranging from about 200 to 2,000 molecular weight units.

Differences in molecular weight ranges in part reflect viscosity and solid content requirements during adhesive application. Spray application methods for flakes, particles or fibers require high solids, relatively low viscosity solutions; property characteristics which are offered by moderate or low molecular weight PF polymers. For solid wood and veneers common usage of roller spreaders, extruders or foaming units allow higher viscosity solutions and hence higher molecular weight PF polymers. Higher molecular weight structures are advanced further and thus should cure faster. In terms of adhesive flow, lower molecular weight polymers are more likely to provide the adhesive penetration required for good bond quality development. In many instances combinations of high and low molecular weight polymers are utilized for wood adhesives in order to achieve formulation with both desirable flow and reactivity behaviour.

$\overline{M}_N$ for UF adhesives appears to be lower than those of PF, with UF plywood resins being about 800 and particleboard or fiberboard resins being near 300 to 400 molecular weight units. The sensitivity of UF polymers to hydrolysis and their tendency to be only partially soluble in aqueous solution has prevented accurate determination of molecular weight distribution for these systems.

Lignin molecular weight and size distribution are highly dependent upon wood species and recovery processes. Acid hydrolysis lignins yield some of the highest molecular weight species because of the extensive condensation reactions that can occur during processing. kraft lignins also tend to have a broad molecular weight distribution range. Organosolv lignins contain much narrower molecular weight ranges but care must be taken in interpreting these values, since they may, in some cases, represent only materials recovered, which may be only a limited portion of the total lignin present in wood.

Techniques used in the isolation of steam exploded lignin have shown that the choice of recovery solvent can lead to a fractionation of lignin molecules. For instance, recovery by organic solvents yields material with $\overline{M}_N$ about 750, while alkali extraction yields greater amounts of materials with $\overline{M}_N$ about 1,600.

Table 11

Molecular Weight Averages and Molecular Weight Ranges for Synthetic and Lignin Polymers*

Material	M_N	M_W	Range of M_W
Plywood PF		2,500	300 - 20,000
Waferboard PF		1,400	94 - 15,000
Particleboard UF		300	200 - 600
Kraft lignin (pine)	1,300 1,190	4,300	1,800 - 55,000
Acid hydrolysis lignin (aspen)	660	10,000	
" (pine)	800	40,000	4,300 - 85,000
Steam explosion lignin (aspen)		5,057	
Acetone extracted	620 - 880	2,300	
Alkali extracted	1,430 - 1,884	7,300	
Organosolv lignin (aspen)	600	2,100	1,500 - 6,800
" (pine)	500	1,400	

* Glasser et al., 1983; Sutcliffe, 1986)

4.2.1.3 Solubility

To achieve uniform adhesive application, polymers need to be soluble and/or well-dispersed within the solvent system. Cost, environmental and clean-up considerations favour "solubilization" in aqueous systems. With PF polymers, aqueous solubility is influenced by the number of methylol groups present, the presence of acid and salt groups and the species molecular weight. Higher methylol contents and lower molecular weights favour increased solubility. To accomodate higher molecular weight polymers present in many wood adhesives, most PF adhesives include strong bases to ionize the phenolic hydroxyl into the more soluble salt form. In plywood adhesives this requires alkali levels approaching 25 percent of phenolic solids, while waferboard and particleboard PF adhesives, being of much lower molecular weights, require levels of less than 10 percent strong alkali. Powdered PF adhesives contain only small amounts of alkali.

Urea formaldehyde polymers tend to be completely soluble in aqueous solutions only at very low molecular weights. In reality a significant portion of the UF molecules is water insoluble but can be readily dispersed in aqueous phase. This gives UF solutions their characteristic white colour.

The high molecular weight and phenolic nature of lignin molecules make them relatively insoluble in aqueous systems unless some alkali is present. The level of alkali necessary again depends upon the amount of very high molecular weight material and the amount of hydroxyl functionality present in the lignin fraction.

4.2.1.4 Thermal Softening

In contrast to aqueous adhesive solutions where moisture provides transfer and wetting of the polymer into the wood surface, powders must first soften through the action of heat and pressure to achieve similar performance. Thus, the physical properties of softening and melt are important parameters for solid polymers. In some cases, when water is removed from a liquid adhesive solution the resulting polymer film also has a characteristic softening point or glass transition to which the glueline temperature must be elevated before proper transfer and wetting can occur. Resin functionality, cross-link density and monomer structure influence the softening point temperature, which is usually determined by volume change or enthalpy change measurements. Table 12 lists softening and glass transition temperatures for PF and a variety of lignin polymers.

The values quoted here should not be taken as absolute, since lignin recovery procedures, and hence lignin yields, vary. In addition, thermal softening temperatures are greatly influenced by the presence of moisture, which acts as a plasticizer. These softening/glass transition values do, however, provide a relative indication of the rheological properties of different lignins compared to phenolic resins.

Table 12

Softening/Glass Transition Temperatures of PF and Lignin Systems*

Material	Softening/Glass Transition Temperature (°C)
PF waferboard powder	42** 55***
Cured PF waferboard powder	160**
Kraft lignin (pine)	169***
Acid hydrolysis lignin (aspen)	95***
" (pine)	96***
Steam explosion lignin (aspen)	139***
Organosolv lignin (aspen)	97***
" (pine)	91***

*(Glasser, 1983)

** Softening point measured compressing sample at 0.25 kpa while heating.

*** Glass transition as determined by differential scanning colorimetry (DSC).

4.2.2 Adhesive Properties

The polymer properties discussed in the previous section have a direct influence on the performance of these materials as adhesives in wood bonding. Hence, comparisons between properties of synthetic polymers and lignin properties provide some insight into the suitability of a particular lignin system for wood bonding applications, while also identifying parameters which may need to be changed in lignin to achieve useful adhesives.

This interrelationship between polymer properties and adhesive performance is illustrated in the following three adhesive parameters important to both the application process and bond performance.

4.2.2.1 Viscosity

As mentioned previously, the equipment used to apply liquid adhesives is highly dependent on solution viscosity. Spray systems normally require low viscosities, while roller applications can accomodate higher viscosity mixtures. Molecular weight, molecular shape, and chemical functional groups all influence adhesive viscosity. Many active sites for polymerization also correspond to functional groups that assist in solubilization. Thus, the polymer system becomes less soluble through both the loss of these sites due to polymerization and through the formation of higher molecular weight species. With most solvent systems, higher molecular weight species are more difficult to solubilize, especially due to entangled, long polymer chains or to the presence of extensively branched chain structures. In aqueous solvent this can result in high viscosity behaviour, especially where extensive hydrogen bonding can also occur. The loss of methylol groups in PF adhesives during condensation polymerization reactions contributes to higher viscosity solutions. Conversion of phenolic hydroxyl groups to the more ionic salt form through addition of NaOH or ammonia results in solubility improvements and correspondingly lower viscosities. With ultra-high molecular weights this ionization technique can only reduce viscosities to a limited extent. In lignin systems both the high molecular weights and the strong association between lignin molecules at moderate solution concentrations result in high viscosity mixtures. Ionization of phenolic hydroxyls can again be used to reduce viscosities. Other possibilities for lowering viscosities at higher levels of polymerization are through reducing solids contents or developing formulations that have sufficiently low molecular weight species to solubilize the higher molecular weight portion of the mixture.

4.2.2.2 Flow and Wetting

Adhesive flow and wetting of the wood surface are important prerequisites for achieving good bond quality. Different molecular sizes and weights directly influence a polymer's ability to wet and penetrate a wood substance. The electronic charge characteristics of the adhesive's molecules are a further factor which can affect wetting. Both factors influence viscosity, which has a direct bearing on adhesive application possibilities.

The synthesis of formaldehyde-based adhesives produces a wide distribution of molecular weight that can fit well into flow and wetting requirements during bond formation. The degree of wetting ability necessary in the adhesive itself varies depending upon the application technique. For instance, in roller applications the mechanical forces and the capillary action of wood fibers can combine to overcome wetting difficulties. A broad distribution of molecular weights allows opportunity for a portion of the adhesive to diffuse a short distance into the wood while, at the same time, leaving the bulk of high molecular weight segments on the wood surface to react and form strong cohesive bonds in the glueline.

Adhesive flow and wetting behaviour are important for two aspects of wood bonding:

- The application stage where an adhesive needs to spread across the wood surface and transfer between adjacent surfaces during blending and prepressing.

- The bonding stage where the adhesive needs to penetrate the first few wood cell layers, flow to further fill out the glueline area, react to bond with the wood and cross-link with other adhesive molecules to form strong stable bonds. This action takes place under the influence of heat and pressure. The presence of moisture and the thermal softening character of the adhesive greatly influence the degree of flow occuring. As described previously, lignins have thermal softening temperatures which fall between a moderately polymerized and a highly advanced PF resin. Thus, heat and pressure used during the bonding processes will cause lignins to flow, but the high molecular weight of most of the lignin species will restrict their penetration into the cell walls to produce strong, durable bonds.

4.2.2.3 Cure Time and Temperature

Press time is a significant factor having an impact on the manufacturing costs of wood composites. Consequently, while low-cost binders are favoured, it is more important to utilize an adhesive that is reliable and fast-curing. Reactivity of synthetic wood adhesives is such that press times in the range of three to five minutes for 12.5 mm thick panels are common at 150 to 210°C press temperatures. Numerous cure studies have shown that alkaline PF adhesives require manufacturing conditions that require glueline temperatures of 120 to 130°C to cure. Urea formaldehyde binders can be cured in a few hours at room temperature or in a few minutes at glueline temperatures of 120°C. Kraft lignin-formaldehyde prepolymers require higher cure temperatures than PFs, often in the range of 150 to 170°C glueline temperatures, with longer press times, often 10 to 30 percent longer. Spent sulfite liquors require similar temperatures and times to cure unless highly acidic conditions, which are detrimental to bond durability, are employed. Similar bonding temperature and time requirements have been reported in limited bonding studies with

organosolv or steam explosion lignins (Calve' and Shields, 1982). It is clear that the reduced number of reactive sites and the limited access to these sites because of steric hindrance on the lignin polymer combine to affect press time and temperature requirements. Consequently the cured lignin adhesive has fewer cross-links and a less homogeneous structure than that of PF adhesives.

5.0 PART III

FUTURE POTENTIAL FOR LIGNIN-BASED ADHESIVES

Lignin, being a renewable natural product available in large volumes and at a moderate cost from pulping operations, has traditionally been viewed as a potential source for aromatic chemicals and adhesives. As described in Part I, attemps to develop adhesives from lignin have been numerous and varied with many reports of laboratory research achievements but only limited success in industrial applications. These have involved either: (1) use of crude lignin solution as reactant; (2) use of purified and/or modified lignins with or without co-polymer reactants; (3) breakdown of lignin structures to monomeric species via pyrolysis, oxidation, hydrolysis, or hydrogenolysis processes followed by reaction of the resulting monomers in a controlled manner to form desirable polymers. Realistically, the third option, because of high energy input required and extensive processing cost, will not be commercially viable in the near future. In the context of the next decade, lignin adhesive developments will still need to address problems associated with:

- non-uniformity of lignin isolated from different mill sources
- broad range of molecular sizes and shapes present in lignin mixtures
- high vicosity of lignin solutions at moderate concentrations
- presence of sulfur, nitrogen and carbohydrate contaminates
- lack of sufficient reactive sites
- higher cure temperature requirements.

Some of these limitations will need to be overcome to successfully utilize lignin adhesives. For a number of reasons, the optimum route for achieving successful formulations in the foreseeable future is most likely through PF-lignin combinations. From economic considerations (see Table 13) lignin-PF combinations can offer substantial cost savings even with moderate lignin costs. Already extensive documentation has established the feasibility of utilizing binders containing over 50 percent lignin for waferboard/OSB panels. Codes and standards requirements and the long-term acceptance of PF systems as being strong and durable is another reason favouring PF-lignin combinations over strictly lignin developments. Finally, from a reactivity enhancement and processing perspective, PF-lignin systems are relatively easy to formulate and manufacture.

The co-polymerization of SSL and kraft lignin with sythetic polymers has been studied extensively. Substantial information has been developed about the chemical and physical structure of these two lignin systems, which has helped in formulating appropriate lignin-synthetic resin co-polymers. Enzymatic and organosolv lignin, in contrast, are not yet well defined. The milder reaction conditions

in these processes do result in lignin solutions relatively free of sulfur and nitrogen contaminates but additional amounts of carbohydrate and enzymatic materials may be present. Adjustments in process and recovery procedures also will yield significant differences in isolated lignin structures. Thus, an important first research priority for future development of enzymatic, lignin-based adhesives is to extensively characterize the chemical and physical properties of these lignin materials.

Bond evaluation data for PF-lignin adhesives have consistently shown these binders to provide good shear strength values but poorer wood failure values than PF adhesives. This result is common for most PF-natural product combinations and becomes more evident together with decreased glueline water-resistance as lignin content increaes. Enzymatic lignins will likely exhibit similar behaviour.

A number of technological developments are available to help overcome many of the limitations of present PF-lignin systems, which also can be applied to common limitations present in enzymatic lignin-based systems. The most relevant areas of concern and corresponding technology which likely will influence lignin adhesive research and development in the near future are as follows:

5.1 ISOLATION AND UNIFORMITY

Between-mill variations in lignins isolated from the pulping stream is a well-recognized factor in lignin adhesive formulations. Some improvement in crude lignin homogeniety can be achieved by selecting material from only a very limited number of mills which pulp one species and have a consistent production flow. Monitoring output through suitable characterization methodology would be of added benefit. Even the best of crude lignin isolates will need further purification.

Fractionation techniques which separate lignin components either on the basis of molecular weight and shape or by solubility will be necessary to improve lignin uniformity for adhesive applications. Possibilities for achieving these separations could be through selective solvent extraction or centrifuge techniques.

Ultrafiltration is a relatively new technology likely to have an important influence on lignin fractionation potential. Standard filtration methods allow particulate material of about 5 to 10 um to be separated while ultrafiltration membranes can separate low and high molecular weight species in lignin solutions. Advancements in membrane materials has led to efficient, industrial-scale equipment becoming available which can accomodate a variety of temperature and pH conditions. The combination of ultrafiltration with electrodialysis techniques should also be explored as a means of improving separation on the basis of both molecular size and chemical functionality.

5.2 STANDARDS DEVELOPMENTS

Panel product codes and standards are undergoing continual revision and expansion to accomodate new processes and service requirements for products. These changes can have a significant impact on product acceptance. A recent example of change is the new waferboard/OSB standards (Anonymous, 1985) which is a more practical document reflecting the current state of the art of these products. While previous standards (Anomymous, 1978) only allowed PF adhesives, the new standard using a substantial data base developed through extensive experimentation establishes test criteria to judge the suitability of alternate adhesives. This development allows additional opportunities for the acceptance of lignin adhesive systems in waferboard/OSB panels.

Further opportunities to utilize lignin-based adhesives will occur as wood product standards are rewritten in terms of performance criteria rather than the product standard philosophy which was favoured when only a few distinct products like plywood and particleboard were produced.

5.3 MODIFICATION TO INCREASE REACTIVITY

Enhancement of the strength and durability of lignin-based adhesives requires lignin structures with a chemical functionality similar to that present in PF adhesives. Increasing reactivity through direct modification of sites on the lignin molecule likely offers the greatest potentioal for developing successful lignin-based adhesives. Various options include alterations to the: phenolic ring, phenolic hydroxyls, phenolic methoxyls, carbonyl side chain groups and unsaturated groups on side chains. From a practical viewpoint, the methodology most likely to be of commercial benefit for improving lignin reactivity are demethylation, catalysis and free radical coupling.

The presence of methoxyl groups on the phenolic ring is a severe detriment to lignin reactivity. This becomes a more crucial problem with steam exploded lignins since this process best suits hardwood species which contain substantially more methoxyl groups. Present chemical means available for demethylation include hydrolysis reactions with strong acids or bases or oxidation reactions with agents such as sodium chlorite, chlorine dioxide, and peroxides. Electrolysis treatment of lignin can also afford demethylated products (Chum and Baizer, 1985). In both these processes, care must be exercised to keep the reactive conditions selective enough to avoid side reactions such as condensation polymerization. Enzymatic and bacterial processes, similar to those present during brown and white rot decay of lignocellulosics, offers and additional means for demethylation (Tai et all, 1982). Drawbacks to these procedures are long processing times and presence of high nitrogen containing enzymatic materials in the final product.

Catalysts for PF-lignin-based adhesives usually are alkaline for reason of mixture, water solubility and control of polymerization. Some opportunities exist for increasing the reactivity of some meta

positions on the lignin phenolic ring by utilizing acid catalyst conditions. Such conditions would greatly enhance polymerization rates and could be of wood bonding utility if acid conditions in the glueline could be neutralized following cure. Further benefits may arise from use of organometallic or oxidation-reduction catalysts.

Both PF and PF-lignin adhesive developments have focussed on ionic or covalent mechanisms for bond formation. Free radical mechanisms are an alternative which could be explored further as a means of polymerizing and curing adhesives. Under highly oxidative conditions (i.e., hydrogen peroxide) lignins can readily lose electrons to form phenoxy free radicals which can couple with other phenolic nuclei to form chain-extended polymers. Evidence suggests this reaction can occur at relatively low temperatures (Nimz, 1983). Certainly adequate means of reaction control and use of less corrosive chemicals would be beneficial to this process.

5.4 APPLICATION TECHNOLOGY

Visosity and solubility problems encountered with lignin mixtures, including some enzymatic types, often can be a serious hinderance to the use of these materials as adhesives. In aqueous solutions, many lignin-based adhesives tend to be two-phased emulsions or dispersions unless highly alkaline conditions are used. New technology (Cone and Steinberg, 1975) for foaming adhesives has potential to utilize these partially soluble lignin solutions. Foaming is accomplished in a continuous manner by mixing air and adhesive in a pressurized chamber under the action of a high-speed stirrer. By this means, small bubbles are dispersed into the mixture which expand several-fold as the pressure drops to atmospheric conditions. The resulting foam mixture is similar in consistency to shaving cream. Commercial equipment (White, 1985) developed for plywood applies these foamed adhesives in the form of ribbons. Surfactants often are needed in these formulations to enhance foam development and foam stability. Lignins have chemical properties which make them suitable as surfactants, while our experience with PF systems indicates that emulsions and dispersions of these type are readily foamable and stable.

5.5 PROCESSING TECHNOLOGY

Both limitations in reactive sites and the high average molecular weight range of lignins are recognized as having a detrimental effect on cure development in lignin-based adhesives. In some cases opportunities may exist to use process technology to improve cure potential. In particular, the steam explosion process has utilized conditions conductive to maximizing carbohydrate recovery. Here, adjustment in treatment conditions (i.e. temperature, time, pressure, catalyst) can greatly alter the type of lignin recoverable. It is conceivable that custom made lignin products be generated which will have more favourable bonding properties. Evaluation of such process variation may help to determine appropriate conditions for optimizing both carbohydrate recovery and ligning bonding potential.

Recent commercial developments in steam presses (Sitzler, 1986) is another technological development of importance to lignin utilization in adhesives. This technique involves direct injection into the wood mate of high pressure steam through small holes in the press platen face. The steam quickly permeates the mat, releasing heat of condensation energy as vapour condenses into wood particles. Consequently, the temperature rise is faster and the heat is distributed more uniformly throughout the mat than with conventional hot pressing.

The efficiency of this process depends upon wood particle size and precise control of steam pressures and injection sequence. For lignin adhesive utilization, steam pressing provides a means for quickly attaining the necessary cure temperatures within the mat core. Tests have established that panels of 12mm thickness could be pressed and cured in about one minute with this technique. Thus, higher lignin content formulations become more practical. An assessment still needs to be undertaken of comparative press time advantages that are possible with various lignin-based formulations.

5.6 SURVEY OF OPINION ON LIGNIN ADHESIVES POTENTIAL IN FUTURE

A limited telephone survey was conducted to determine current opinions of persons in industry or research institutions involved in lignin uses in adhesives. While this survey produced varied comments the reader should recognize that the feedback obtained represent personal opinions and bias. They may not accurately reflect a company research policy since management view is not represented and in some cases real intentions may not be given.

Comments obtained can be summarized as follows:

1. Borden Co., Toronto Otto Udvardy, Group Leader

   This company is not engaged in research on the use of lignin as an adhesive at the present time. Although it is felt that there is a potential for the use of lignin-based adhesives, the company has no plans for future work in this field.

2. Borden Chemicals, Vancouver, B.C. Dr. Chiu

   The company is active in research on lignin as an adhesive, both lignosulfonates and kraft lignins. Dr. Chiu believes there is a future for lignin-based adhesives in combination with PF resins for use as particleboard or waferboard adhesives. Of course, much will depend on the cost of phenol. He does not know of any group in the country active in this field.

3. Reichhold Chemicals, Ste. Therese, P.Q. D.A. Go

   The company is doing work in the field of lignin as an adhesive but would not release information on the nature of that work or on how much money is being spent for that purpose.

4. Reichhold, Vancouver, B.C. Mr. W. Ainslie, Manager

Reichhold is active in the field of lignin-based adhesives, using both lignosulfonates and kraft lignin in combination with PF as an adhesive for particleboard and waferboard. Mr. Ainslie believes there is future potential for the use of lignin in adhesives especially if the price of phenol increases. Also, much depends upon the extent of the modifications to the lignin molecules required to increase their reactivity.

5. Bakelite Thermosets Ltd., Ontario Mr. Wideman

The company is doing very little work in this field, but believes in the potential of lignin as an adhesive.

6. Reed Paper, Chemicals Division, Quebec City, Dr. Goel

The company is doing work on the use of lignosulfonates mixed with phenol-formaldehyde resins as adhesives for particleboard and waferboard production. Dr. Goel could not give figures as to lignin costs, which vary from process to process. He believes that lignin has a future as an adhesive.

7. Tembec Inc., P.Q. Dr. Bialski, Research Director

The company is not doing much work on the use of lignin as an adhesive. Claims that up to 30 percent lignosulfonates, at least, mixed with phenol-formaldehyde (PF) resins would have to be used for particleboard adhesives. He mentioned the use of lignosulfonates mixed with urea-formaldehyde resins although there is a compatibility problem and the greatest savings would be achieved with PF resins. Sees limited future for the use of lignin as an adhesive.

8. Pulp & Paper Research Institute, Pointe Claire, P.Q.
Miss C. Luthe

The institute is active in this field. Work so far has been with lignosulfonates. Miss Luthe believes there is good potential for the use of lignin-based adhesives. Does not know of any research group involved in this type of research.

9. Jim Walters Research, Tampa, Florida George Grozdits

At the moment, no work is being done on lignin as an adhesive. Grozdits feels there is good possibility for the future use of lignin as an adhesive. The use of lignin should not be confined to particleboard and waferboard production but should be extended to other material such as cement binders, fiberboard, etc.

10. U.S. Forest Products Laboratory, Madison, Wisconsin
Dr. Gillespie

Some work is being carried out at Madison exclusively on the use of kraft lignin as an adhesive. Dr. Gillespie thinks there is a future for lignin as an adhesive but feels that this is still far away. Madison wants to be ready with a lignin-based substitute if the cost of phenol (petroleum) increases.

5.7 ALBERTA'S AND CANADA'S R&D CAPABILITIES IN THE FIELD OF LIGNIN BASED ADHESIVE DEVELOPMENTS

Based on our knowledge and information gained from several university and industrial sources, Alberta's R&D activity in the field of lignin is limited. In recent years some studies on Aspen lignin separation and identification have, in part, been carried out by N. Cyr of the Alberta Research Council. In addition, Tigney Technology was at one time utilizing a steam explosion technique, similar to the Masonite gun process, to treat Aspen wood in order to separate cellulose fiber or saccharification material from lignin. Substantial development work on this process was originally undertaken by Iotech and Stake Technology, two Ontario based companies.

While few research projects on lignin are presently being funded in Alberta, there exists individuals and organizations capable of working on lignin within the province. This potential expertise is likely available at the Alberta Research Council in their chemical and analytical divisions and at the University of Alberta at Edmonton in the faculties of Chemical Engineering and Forestry and Agricultural Resources.

From a Canadian perspective, Forintek Canada has the most extensive R and D program in both biotechnology and adhesive development aspects of lignin. This experience extends over a twenty year period. The Pulp and Paper Research Institute of Canada also has continual on-going programs on the utilizing lignin for a variety of products. Adhesive companies' like Bordens, Reichhold and Bakelite Thermoset all have developed some form of lignin-PF adhesives based on readily available SSl or kraft lignins. Tembec Inc. of Quebec also has some expertise in SSL modified PF systems.

Within Canadian universities, all major chemistry, chemical engineering and forestry faculties should have the personnel to conduct some research on lignin separation and characterization.

6.0 CONCLUSIONS AND RECOMMENDATIONS

Large quantities of lignin are presently produced by conventional pulping processes while in the future steam explosion and organosolv treatments of lignocelluosics likely will be an additional source of lignin materials. With proper production controls and costs, lignin output from a few of these plants could readily supply the adhesive needs of the wood industry if appropriate lignin adhesive formulations could be developed.

Numerous research studies have been undertaken with the objective of producing a lignin adhesive. To date, results have shown several promising formulations in laboratory trials but with only very limited commercial success. Some reasons for these difficulties can be attributed to:

- non-uniformity of lignins obtained from pulping operations
- lack of reactive sites in lignin
- solubility and application problems
- higher cure temperature and time requirements
- limitations of codes and standards

Frequently, lignin adhesives do not attain the reactivity and processing properties present in PF adhesive systems. Because of these limitations, the commercial use of lignin as an extender or as a co-reactant for PF wood adhesives is closer to realization than the use of lignin alone as a wood adhesive. The cost saving to plywood and waferboard manufacturers is the main driving force. Consequently, the best opportunity for utilizing lignin as an adhesive in the near future is through PF-lignin combinations, especially if the lignin component can be made more uniform and reactive.

Opportunities for additional lignin usage is UF systems also are likely in the near future. These will correspond more to situations where enhance durability or reduced formaldehyde emissions are desired. The amount of lignin incorporated into UF systems will be limited by how much cure time increase can be tolerated and by the importance of retaining a light coloured glueline.

Both PRF and isocyanates are reacted and relatively expensive adhesives. Future possibilities for utilizing large volumes of lignin in these systems will be limited because of the concern for retention of superior adhesive properties at moderate cure temperatures. Even small amounts of lignin substitution however, will have a significant effect on adhesive cost.

Steam explosion and organosolv processes offer promise of lignin sources with greater uniformity, lower average molecular weight and free of sulfur and nitrogen contamination. A major impediment, however, is the limited characterization of these lignins and how process variates influence recoverable lignin types. It is probable that these lignins will require modification similar to those needed for kraft lignins in order to generate quality adhesives.

Of the various research options available, it is important that both chemical and processing technology to the development of lignin-based

adhesives be addressed. Based on the analysis undertaken for this report, it is concluded that research priorities be directed towards:

- full characterizing lignin products obtained from steam explosion chemical thermomechanical, or organosolv processes under varying reaction conditions.

- assessing and/or developing means of fractionating different molecular weight components of lignin on a large scale.

- identifying and examining effective chemical and electrochemical means for demethylating lignins to enhance reactivity.

- study of alternate catalyst systems for lignin plymerization, in particular the use of acid catalysts and free radicals.

- identifying and utilizing appropriate application and process technology to aid the development of adhesives from different lignin sources.

- assessing steam pressing as a mode of improving lignin based adhesive cure times.

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